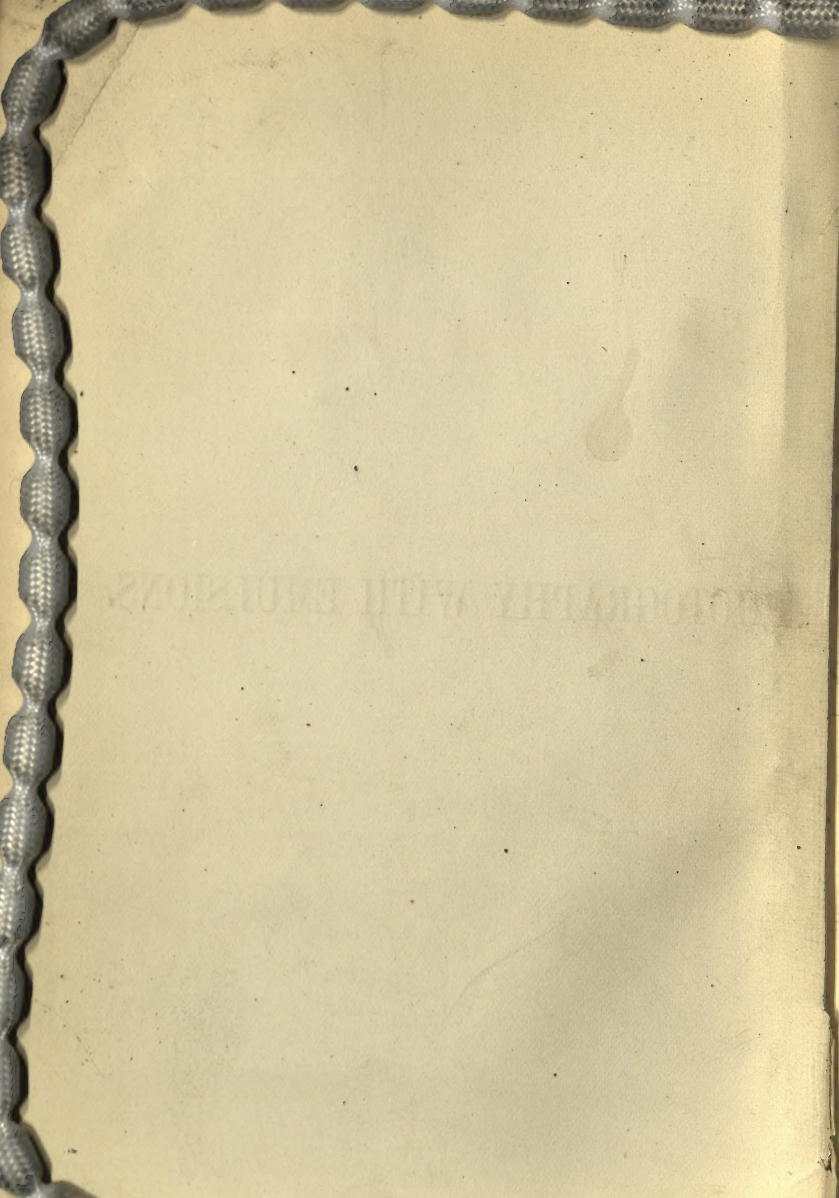


PHOTOGRAPHY WITH EMULSIONS.





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PHOTOGRAPHY WITH EMULSIONS.

A TREATISE ON THE

THEORY AND PRACTICAL WORKING

OF THE

COLLODION AND GELATINE

EMULSION PROCESSES.

BY

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LONDON:

PIPER & CARTER, 5, CASTLE STREET, HOLBORN, E.C.

1885.

LONDON:
PIPER AND CARTER, CASTLE STREET, HOLBORN, E.C.



PREFACE.

ANOTHER Edition of this work has been called for by the Publishers, and, in preparing it, the Author has endeavoured so to re-arrange and prune the older matter, and to insert new, as to make it useful to those whose knowledge of chemistry may be limited, as well as to those who are experts in that far-reaching science. Again, there are many who at present care nothing about theory, and who regard practical results as their sole aim. An endeavour has been made to meet their views as well, by, as far as possible, confining all theoretical considerations to those chapters which are marked with double asterisks in the table of Contents. These chapters may be omitted without in any

way interfering with the practical part of the subject. Those readers who prefer to buy their dry plates in the market to preparing them themselves, may omit the chapters marked with a single asterisk.

The Author feels that there must be many shortcomings in the book, although he has tried to keep it up to date. One thing, however, he may add, that there is no process stated in it which he has not thoroughly tried, and no theory which is given which he has not endeavoured to confirm or refute experimentally.

W. DE W. ABNEY.

South Kensington,

September, 1885.



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PHOTOGRAPHY WITH EMULSIONS.

CHAPTER I.

PRELIMINARY CONSIDERATIONS.

THE term emulsion is derived from the Latin word "emulgere," to milk out, and the definition of it as found in the dictionary is, "any milk-like mixture prepared by uniting oil and water by means of another substance." For our photographic technology this is hardly a correct definition, for by it we mean a sensitive salt of silver in very minute division, held in suspension in some viscous body, such as gelatine, or, very often, collodion.

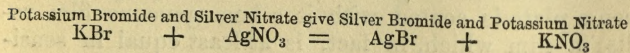
An emulsion in its most elementary form may be considered to be simply a pure silver haloid held in suspension in collodion or gelatine, and so well prepared that when a plate is coated with it, a homogeneous film results; a film which, in fact, is at least equal in sensitiveness and in physical qualities to any which can be prepared by any other process.

Emulsion processes are divided into two classes: one in which the emulsion is made up and used without any preliminary extraction of the soluble salts which are necessarily present in their manufacture, owing to the

double decomposition of the salts employed, and the silver nitrate; and the other where these soluble salts are extracted. In the first process the plates are washed after coating, and is usually confined to collodion emulsions; whilst in the second they are coated, and generally left to dry spontaneously.

All emulsions at present in vogue for making negatives may be considered to be simply bromide of silver, since it is the basis on which all alterations by the addition of iodide or chloride are to be made. It will be seen in the context that these additions are not unimportant as regards the range of sensitiveness.

The almost universal mode of producing an emulsion is to dissolve certain soluble bromides (such as potassium bromide) in the collodion or in a gelatine solution, and then to gradually pour a solution of silver nitrate dissolved in alcohol and water in the first case, or in water alone in the second, into the viscous fluid, by which means solid bromide of silver is formed, together with a soluble nitrate (such as potassium nitrate). It is this latter soluble product which in washed emulsions is removed, since, if a film be left to dry without eliminating it, crystallization sets up, and the surface of the coated plate is spoilt. Silver chloride is readily emulsified in the same way, substituting a soluble chloride (such as of sodium) for the soluble bromide. Silver iodide is also easily formed into an emulsion in gelatine, but it is formed with much more difficulty in collodion. We give the chemical equation for the formation of silver bromide.



Bromide of silver may be produced in several molecular states, all of which have different degrees of sensitiveness. When we say different molecular states, we mean that the silver bromide has precisely the same chemical composition, but that it is altered physically, the molecules

being larger in some cases than others; the particles are built up of a greater or less number of primary molecules, according to the rapidity of the formation of the solid, and its subsequent treatment by heat, ammonia, &c. Thus, it is known that white light, when transmitted through a film composed of gelatine, in which these particles are suspended, may appear of a ruby, orange, green, purple, or grey colour; and of these, three seem to be different states of molecular aggregation—viz., ruby, green, and grey; the others are probably mixtures of one or more of the three. We must assume that the reader is aware what a spectrum is. By exposing any of these modifications to its action, we find that the range of sensitiveness to the different coloured rays is varied. Thus

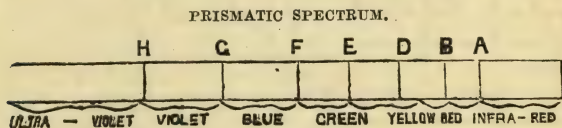


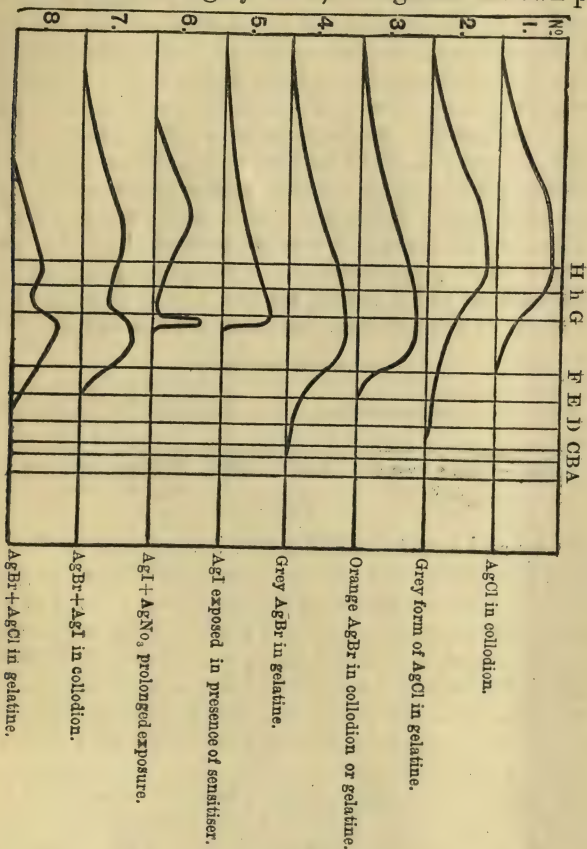
Fig. 1.

the ruby and orange modification is sensitive to the ultra violet, the violet, and blue rays, and a little to the green; the grey blue is sensitive to the same rays, but more strongly in the green, whilst it is able to be impressed by the yellow and by the red rays; the green modification, when in collodion, is sensitive to the ultra-violet, the blue, very slightly to the green, and much more so to the red, and infra-red regions—that is, those dark rays which are miscalled the heat rays.

In fig. 2 the range of sensitiveness of two of these modifications (Nos. 3 and 4) is shown, as well as that of some other salts of silver. The comparative sensitiveness to different parts of the spectrum is shown by the height of the curves.

In collodion emulsion the ruby and orange form of bromide is that most sought after, whilst in gelatine emul-

sion the form which is supposed to give the most sensitive films is the blue grey form; though for our own part



we consider that a tinge of yellow is essential to get the highest sensitiveness. The reason for selecting these forms we shall touch upon by-and-bye.

Iodide of silver in its pure state is sensitive only to the ultra-violet, the violet, and the blue rays, and it may well be supposed that by adding iodide to the bromide, some modification of the range of spectral sensitiveness must be found. Such is the case, and it is more marked in gelatine emulsion, in which, were no iodide added, the emulsion would take the blue grey state (see fig. 2).

The addition of chloride of silver to the bromide modifies the photographic qualities of the latter but little, and since it is but rarely used in any quantity, we need not consider it.

When white light is allowed to act on chloride of silver for a sufficient time to blacken it, in the presence of moisture, or moist air, as is all air unless chemically purified, chlorine is given off. That this is the case is never disputed, its proof being as old as 1780, when Scheele made his classical experiments. We think also it will be allowed that when bromide of silver is acted upon similarly, bromine is given off; a bromide plate when darkened absolutely smells of bromine, or some compound analogous to it. Let us take chloride of silver as the example on which to found an argument, for any reasoning which may apply to the one will equally apply to the other principal haloid salts of silver—viz., the bromide and iodide. Homogeneous matter is made up of molecules, all having a similar composition, and such molecules are themselves made up of atoms. In the case of bromide of silver, for instance, the atoms are bromine and silver. Now we are told in most text-books that silver is a monad,* and that it requires only one atom of bromine to combine with one atom of silver; confining ourselves to pure chemistry, without any reference to photographic action, the evidence of this is based on the behaviour of silver when combined with certain other elements.

* The opinion, however, that silver is a monad is not absolutely allowed by some chemists.

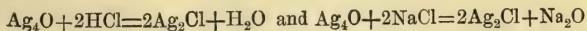
The molecule of chloride of silver is, however, we are constrained to believe, made up of at least two atoms of silver and two of chlorine, and the question arises as to what substance is left behind after the chlorine has been dissociated from it by the action of light. Does such a body as a sub-bromide or sub-chloride exist? Now we will not go into photographic evidence, but confine ourselves at first to chemical evidence simply. In 1839, the year when Daguerreotype was discovered, Wöhler found that if hydrogen was passed over argentic-oxalate, mellitate, or citrate, when heated to the boiling point of water, half the acid was set free, and a dark brown argentous salt remained. The acid could be removed by washing, only a small portion of the argentous salt being removed, the solution of the latter forming a port-wine coloured liquid.

Further, Wöhler obtained argentous oxide (Ag_2O) by means of repeatedly boiling soda-ley with argentic arsenite,* and Geuther found that argentous oxide is formed by precipitating silver nitrate with cuprous hydrate. Again, argentous oxide is produced by the action of hydrogen peroxide on metallic silver. A bright silver plate immersed in a neutral solution of hydrogen dioxide becomes covered with bubbles of oxygen, and coated with a greyish white film, while part of the silver is converted into hydrated argentous oxide, according to the equation— $2\text{Ag}_2 + \text{H}_2\text{O}_2 = 2\text{HAg}_2\text{O}$. Argentous salts are also produced by passing hydrogen into ammoniacal solutions of silver salts.

Such is an outline of the chemical evidence of the existence of argentous oxide, and it would appear that such evidence is very strong—in fact, as strong as required under any circumstances. That this is not the work of only one chemist adds more weight to the existence of such a compound.

* Argentous oxide is, of course, the base of argentous citrate, oxalate, or mellitate.

Such being granted, the admission of the possibility of the existence of sub-chloride or sub-bromide of silver is at once apparent. Wöhler describes a method of preparing it by adding to the argentous oxide a solution of hydrochloric acid, or of common salt. In this case we have :—



Argentous chloride is also said to be formed by bringing silver in contact with a solution of sal-ammoniac, as is also the case by the first action of ferric chloride or cupric chloride. The argentous bromide (sub-bromide) can be formed in the same way. By chemical analogy, if there is such a substance as the sub-oxide or argentous oxide, there is the same reason for believing in the existence of the sub-chloride and sub-bromide. Now comes the question as to whether the same compound is produced by the action of light.

When silver chloride is exposed to the action of light, we know well that a violet-coloured substance is produced, and that such a colouration is also found when exposure takes place in the presence of nitric acid. We also know that the metallic silver dissolves in dilute nitric acid. Now, since chlorine is evolved, one of two things must occur: either the total liberation of the chlorine from the silver salt, or else its partial liberation. Which does it do? Under any ordinary circumstances it would be said that it was not metallic silver which was left, since it was unacted upon by nitric acid; however, there are those who will accept a conclusion derived from one isolated fact. Some thirty years ago or more, Guthrie experimented on this subject, and he put it down that metallic silver was formed, but that it was in a passive state, similar to that state which iron takes. The connection between the two is not, however, very apparent.

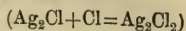
He found that the substance he got in every case of the darkened chloride was insoluble in nitric acid, but that

after treatment with ammonia the residue was soluble. This is exactly the behaviour of chemically produced argentous chloride, and is a striking proof that the light-produced compound and this are identical.

It is usually said, if silver bromide be exposed to light in nitric acid, that no change takes place in it—*i. e.*, that it remains as silver bromide. Now, to test this, silver bromide was exposed to light in strong nitric acid, and subsequently the acid was treated with silver nitrate. A faint precipitate of bromide of silver immediately showed. If dilute nitric acid be used, the silver is dissolved from the sub-bromide almost at once.

Now we have an exceedingly interesting proof that the salt formed by light and the argentous chloride are the same, independently of chemical proof. If a collodion film containing silver chloride be exposed to light till it is lavender, and be then exposed to the action of the spectrum, we get a coloured representation of that spectrum. Further, if a similar film be exposed to light, and the silver be reduced to the metallic state by a developer, and it is then immersed till it assumes a grey colour in ferric chloride or cupric chloride, the same colourific action takes place; or, again, if a metallic silver plate be treated in the same way, we have a coloured spectrum. It would be curious that such should be the case if the compounds are different.

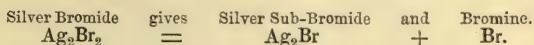
The amount of the chloride converted into the coloured salt, compared with the total amount to which a prolonged exposure to light is given to produce it, is small, perhaps not more than five per cent.; but it must be recollected that chlorine as it is liberated from the chloride by light has always sub-chloride besides it, and it is always more probable that a larger percentage will combine with the sub-chloride and form chloride



rather than escape. For this reason there is no difficulty in reconciling fact with theory.

We may mention that Dr. Hodgkinson, by exposing a large quantity of chloride to light, has been able to isolate the sub-chloride by treating the mass with sodium chloride solutions, which are able to dissolve the chloride without destroying the sub-chloride, which remains insoluble.

We may now assume that the prolonged action of light is to reduce the haloid to a simpler type, which we may call the sub-haloid. Thus—



It is a pertinent question to put as to whether the visible and the invisible (or developable) image are of the same nature; which may be answered by another question: Can the line be drawn where the image is invisible? If so, what is the boundary between the two? If we admit the theory of the formation of the visible image, it seems hardly logical to deny a similar formation for the invisible or photographic image. It is quite possible that beings with more acute sight than ourselves might be able to see the image which we cannot. As we know, certain insects can hear sounds which do not affect our auditory nerves. Coloured particles are visible when put together *en masse*; but if only a few coloured particles are present in a mass of colourless particle, it is quite certain they may remain undetected. If we take a couple of plates, and coat them with emulsion, and place them in some conducting solution, connect the films with a very sensitive galvanometer, and allow light for a second to fall on one plate, there will be a deflection of the needle, showing that chemical action is taking place on it; expose for a time sufficiently long to discolour the film, and the same result occurs. There is chemical action, then, in both cases: what is the difference between the two? The chemical theory of the photographic image is based upon the fact that where light of a proper kind acts on a molecule the atoms are

made to swing, however short be that exposure. If it be for a second, the average number of vibrations which light of a mean wave length makes is somewhere about 700 million millions, a goodly number, and which, if the blows from the ether be well timed, is sufficient to make an atom of chlorine or bromine fly off from the molecule, or, in other words, sufficient to make it swing out of the sphere of molecular attraction, particularly if some other molecule is near which is ready to abstract it and incorporate it with its atoms, and so to form a new body.

Let us stop and see whether such is the practical, and not theoretical, action. Take bromide of silver emulsion in collodion, which latter, when pure, is almost an absolutely neutral substance, and what occurs when it is used dry? It is sensitive to a certain extent; but add some bromine-loving preservative to the film, and the increase of sensitiveness is much increased. If the condition of the bromide under the action of light were merely change in the arrangement of the atoms, but not a chemical change, there would be no use in the bromide absorbent, and it ought to be positively detrimental.

Let us take another example still of this. If a washed iodide of silver emulsion is prepared with excess of iodide, and a plate be prepared and exposed, no image is developable. Dip half of such a plate into a solution of tannic acid or beer, and develop; the half that has an iodine absorbent will develop after exposure to light, the other half will not. The chemical theory of the photographic image which assumes the liberation of an atom of bromine from the bromide, explains it immediately.

One of the most remarkable proofs of the truth of this theory is found in the explanation of some experiments made by the author on the effect of the spectrum on mixtures of the haloid salts of silver, an account of which is published in the "Proceedings of the Royal Society," and

a diagram of which is seen on page 4. It is there shown, if you have a mixture of pure and dry iodide and bromide of silver, and expose it to the spectrum, that at the place where the iodide alone would show the greatest action on development, the image on the iodide has been destroyed by liberation of bromine from the bromide, which is in contact with it, and which is also acted upon by rays of the same refrangibility. Now no mere physical theory of the photographic image would account for this. If a mere change in the arrangement of the atoms took place, instead of the developed image being almost *nil* at this particular part of the spectrum, it would be increased in intensity, and such increased intensity is to be found if a halogen absorbent is in contact with them.

We will merely mention that one form of the physical theory of the formation of the photographic image is that the light sets up vibrations, and that whilst no chemical change is wrought, yet that it is the increased vibrations which give the developing power, and that when the vibrations cease the image is non-existent. This is one of those pretty ideas which have to be relegated to the same limbo as perpetual motion. We hear of a gelatine plate being exposed and developed with unimpaired vigour after a lapse of twelve or twenty months. We ourselves have kept gelatine plates a year, and developed some of them every three months. These plates were exposed behind a sensitometer, and kept to ascertain if there were any fading of the image. Plates which gave 22 on the sensitometer at first, after the lapse of a year gave an image showing 21. Hence, to accept this theory, we should have to conclude that the vibrations commenced at a certain time, kept of the same amplitude, or nearly so, for the space of a year. If a collodion plate is treated in the same way, the image will die out much more rapidly. A couple of months is sufficient in most cases to obliterate nearly every trace of an image, and yet it is the same material acted upon in both cases. Why should it act

differently in the two cases? The answer is somewhat hard on the vibration hypothesis, but it is perfectly easy on the chemical theory of the photographic image. Exposure to the atmosphere, or to a substance which can oxidize the image, we have shown destroys the developing capacity of the image, and the difference of the enclosures of the bromide when in the gelatine and collodion fully explains the reason why the destruction is more rapid in the one case than the other.

Again, we can absolutely show that if increased amplitude of vibration be given to the atoms of a bromide plate, such vibrations subside rapidly. If we take a hot iron and press it to the back of a gelatine plate, and expose the latter to light whilst hot, and then, after cooling, develop the plate, we get an image of the iron shown by increased blackening of those parts which were in contact with the glass heated by the iron. If, however, the hot iron be applied to the back of the plate, which is then allowed to cool, and if, after such cooling, it be exposed to light, no trace of the iron shape is visible; the silver salt has returned to its normal condition.

In the one case, we have the amplitude of the vibrations of the atoms of the molecules (which, when at any temperature presumably above the absolute zero, are always vibrating) increased by the application of the hot iron, but not sufficiently to make them separate entirely. Where light of proper colour impinges on these atoms, which are already swinging with increased amplitude, they are more readily swung off than when it has the whole of the work to perform upon them, and as a result we have the image of the flat iron shown by the increased number of molecules which have been de-atomized. In the other case the plate is heated, and the increased amplitude of vibration must still be there, and, according to the vibration theory, should continue; but the fact is, that it does nothing of the kind. The atoms resume their normal swing when the plate is cold. It is for those

who hold the physical theory of the formation of the photographic image to explain why the increased amplitude, due to the heating, dies away, whilst that due to light does not. The chemical theory, then, fully accounts for these experiments, which, as far as we are aware, no other theory can do.

CHAPTER II.

ALKALINE DEVELOPMENT.

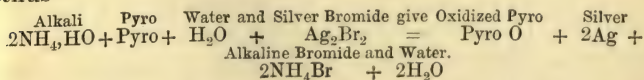
It will be noticed that all emulsion plates are developed either by alkaline development, or by ferrous oxalate development, and we propose to consider these two developers from their theoretical point of view. It may be said, first of all, that iodide is not readily amenable to alkaline development, and we therefore do not consider it; the bromide and chloride are the salts which are chiefly employed, and it is their part in it we shall consider.

An alkaline developer consists of a strong absorbent of oxygen, an alkali, and a soluble bromide or chloride. The two first are the only essentials for the reduction of a salt of silver to the metallic state. Thus, if we take precipitated bromide of silver,* and add to it a solution of pyrogalllic acid and ammonia, we shall find that it is rapidly reduced to the metallic state. If, however, we precipitate the silver bromide in the dark, and add to the developing solutions a little bromide of potassium, we find that the mass is reduced more slowly, the soluble bromide acting as a retarder to the reduction. If we have a film which has been exposed to a camera image, and develop by the

* Precipitated by dissolving a little bromide of potassium in water, and adding to it silver nitrate, and then washing.

unrestrained solution, we shall find, as a rule with gelatine films, and always with collodion films, a reduction all over the surface; whereas, if we use one containing the restrainer, we shall find that the image develops properly. Whenever there is a reduction of the silver salt there is an alteration in the developing solution, due to a chemical change in it.

Now what does this reducing action depend on? In the alkaline developer, we repeat, we have three effectives (putting on one side the water, which enters into all three), viz., the pyrogalllic acid, the alkali, and the restraining bromide. When pyrogalllic acid is mixed with an alkali, it is in an unstable state, and greedily absorbs oxygen from whence it can get it. During the process of development it is in contact with water, and with haloid salts of silver—viz., the bromide and the sub-bromide. Take the former into consideration first, leaving out the action of the restrainer, viz., the soluble bromide. We then have a vigorous oxygen absorbent, and a haloid salt of silver and water. Now, all bodies when mixed together have a tendency to enter into new combinations, which take the most stable form they can. This is what the three substances do. The oxygen absorbent will take up oxygen from the water, which, at the moment of liberation, reduces the silver bromide to the metallic state, and the liberated bromine forms, with the hydrogen, hydrobromic acid. This, in its turn, forms bromide of the alkali and water again. Roughly, it may be expressed thus—



So far, we have treated merely of the reduction of bromide of silver (Ag Br_2), and not the sub-bromide (Ag_2). Now the action of light on the bromide (Ag_2Br_2) is to cause one atom of bromine to swing off, and in doing this a certain amount of work has been performed by the

light itself; and that being the case the reduction of the sub-bromide ought to be more easily effected than the bromide. In other words, light has partially effected on the silver bromide what the chemical action of development has to do when light has not acted. Suppose, then, we have an amount of work to be done on the bromide in order to reduce it to metallic silver of (say) 100 units, and that light does 20 of these units, evidently chemical action of developing has only to do 80 units. So if we have bromide and sub-bromide of silver together, and arrange that the chemical energy of the developer shall be (say) 95 units, the developer would be able to reduce the sub-bromide and not the bromide; and in case the energy of the developer was more than 100 units, it would attack the sub-bromide in preference to bromide. With a very weak developer this is the case, and it may be used without any (what is termed a) restrainer. Now what is the action of the restrainer? This is a point which is more difficult to answer. We were now talking of a chemical restrainer, viz., the soluble bromide. Silver salts are known to form double salts very readily. For instance, there are double chlorides of silver and sodium, and they can be obtained in definite crystals, as can the double bromides, and it seems more than probable that the restraining action is due to this affinity. When we have double salts formed, the energy of their combination is shown by the heat which is given out during the combination. Now, in order to dissociate them from each other, work would have to be done on the double molecules; in other words, the work that the two do in combining, which is shown by a rise in temperature, the same amount of work would have to be done on them to separate them. The double salt is, therefore, more stable than the bromide salt *per se*. The energy existing in the developer has not only to do the work of separating the bromine, but also of separating the double salt. It may be said in objection to this that the bromide is in solution,

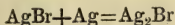
and therefore cannot form a double salt. That would be valid if we could say that no double salt was formed. We know, for instance, that two salts when in solution will form a double salt, and that two solids form a double salt. The question as to whether a salt in solution, such as potassium bromide, can form a double salt with a solid, such as silver bromide, is not quite so easily answered; but the evidence, as far as it goes, is in its favour.

In some electro-chemical experiments which we are undertaking, the formation of a double salt seems to be confirmed, and, as we have said, the temperature test certainly favours such an idea. It must be quite understood that this is not put forward except as a good working hypothesis, which, so far, is uncontradicted by known facts. It may be found to be due to some other cause, though we believe not.

We thus lay the action of the restrainer to the formation of a double salt during development, and a consequent increase in work that the developer has to perform to reduce it. A body like the sub-bromide does not appear to form double salts; its composition is not allied to the soluble bromide. Now it may be taken that solubility of the one body in the other is indicative of the possibility of the formation of the double salts. Dr. Hodgkinson finds that whilst the chloride of silver is soluble in sodium chloride, the sub-chloride is not, and thus he arrives at a method of separating the two. This points to a similar action of the bromide and sub-bromide in soluble bromide, or it must not be forgotten that bromide of silver is soluble in bromide of potassium to a limited extent.

We have so far treated of the action of pyrogallic acid alkali restrainer, or the bromide or sub-bromide of silver; but there is a further action in development that has to be considered. The quantity of sub-bromide to be reduced is infinitesimally small when the brief exposure to light alone produces it. The first act of the developer is to reduce the sub-bromide, but at the same instant that

the metallic silver is formed this metal combines with the silver bromide in contact with it, and fresh sub-bromide is formed, which is then acted upon, and a visible image is produced. The mere fact of a chemical restrainer being used, however, retards development, since the metallic silver first deposited by the development of the sub-bromide has, before it can combine with the adjacent bromide, to undo the double salt, and as this is work to be performed, the development is of necessity slower. Thus, silver and silver bromide yield silver sub-bromide; or,



There are two kinds of restrainers: one chemical, and the other physical. We have treated of the former; now as to the latter.

A physical restrainer is one by which the developer is deprived of rapid access to the exposed sensitive salt, and this is particularly the case when an emulsion is prepared in gelatine. In this state the colloidal nature of the gelatine permits only a very slow access of the developer to the embedded salt. In other words, the small portion of developer which attacks the particle is obliged to attack that portion of it which is more readily reduced, and in the case of gelatino-bromide films, that is the sub-bromide. Albumen acts in the same way, and a physical restrainer is used when with the developer are mixed solutions of gelatine or albumen.

It is thus evident that if an absorbent of oxygen, which by itself is capable of reducing the sub-bromide at the first shock without reducing the bromide, must be a better agent to use than pyrogallie acid, which requires a restrainer. Such an oxygen absorbent has been found by the writer in hydrokinone, which, under ordinary circumstances, has no tendency to reduce the silver bromide, and it has a greater affinity for oxygen than any known organic substance.

From chemical analogy it may be assumed that the

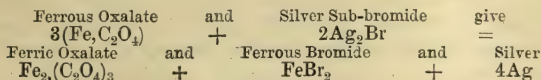
molecular attraction of the metallic silver is strongest at the instant of its reduction. With the weak alkaline developer the silver is reduced but slowly from the *bromide*, and hence it becomes less "nascent," if we may use the term, than it is when it is rapidly reduced. It is found from chemical analysis of the developer after it has been used, that a weakly alkaline solution is only capable of reducing a small amount of the bromide compared with a concentrated solution; in other words, whilst the same amount of ingredients possess the same amount of total energy, yet when diluted the time taken to use up the energy is longer than with more concentrated solutions, and thus the energy applicable at each small interval of time is less in the former than in the latter case. If we strike a moderately rigidly fixed target with a hundred bullets fired at intervals of a minute, we should not expect to overthrow it, but if the 100 bullets were fired all together, and with the same velocity, the united energy of the bullets might probably cause the target to be laid low. In both cases the total energies applied are the same, but the effects are different. In a rough way we may apply this simile to the weak and strong developers when acting on the silver salt.

It will be observed, that various formulæ are given for alkaline development; in one ferro-cyanide of potassium is mixed with the pyrogalllic acid, and in another sulphite of soda. The value of these appears to be either that they form a new compound, or that they absorb oxygen. In any case, the longer the pyrogalllic acid remains unoxidized, the more effectual should be the development.

The hydrosulphite developer may be classed amongst the alkaline developers.

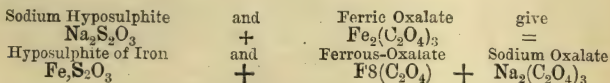
We next have to consider the ferrous-oxalate developer, and it matters but little, as regards theoretical considerations, as to which way it is formed. It will be seen by the formula given later that the ferrous-oxalate developer is in reality a solution of ferrous-oxalate in neutral

potassium oxalate. The latter salt exercises no developing action, but is rather a retarder to development than otherwise. We have therefore only to consider the action of ferrous-oxalate on silver sub-bromide, and it may be expressed as follows :—



By which it will be seen that a metallic bromide is formed, together with ferric oxalate. This is subject again to a change with the potassium oxalate, ferrous-oxalate and potassium bromide being formed.

Experience has shown the writer that the addition of a small quantity of hyposulphite makes development much more rapid, and that a gelatine plate requires less exposure with it. Let us trace what happens to the ferric salt formed :—



We thus find that the ferrous hyposulphite and oxalate are formed, and also a sodium oxalate. It seems likely that the destruction of the ferric salt immediately on its formation is one cause of the increased activity of the developer. The ferrous citrate, ferrous citro-oxalate, and ferrous tartrate act, chemically, in the same way as the ferrous oxalate.

CHAPTER III.

THE CAUSE AND CURE OF FOG IN EMULSIONS.

EVERY student in emulsion work has found, and will find, that the chief obstacle that he has to overcome to obtain success is the tendency for the plates prepared with an emulsion to fog, or veil over on development, and it has taken a great deal of experimental work to enable it to be overcome. The writer ventures to think that the researches he has made on the subject have explained in a great measure, if not entirely, its *raison d'être*.

Setting aside the collodion or gelatine from the question, and merely taking into consideration the sensitive salts employed, we may arrive at very definite results. It has been asserted that a neutral combination between two substances can never take place; for example, if we mix potassium chloride with silver nitrate we shall never be able to get pure silver chloride, however much we may wash it—that either the soluble potassium or silver salt will always be in excess, though probably in the minutest quantities. This certainly is the case theoretically, because do what you will, and wash as long as you like, there still must be some infinitely small part of the soluble salt left behind. Now, in ordinary chemical analysis, where products have to be weighed, the residual impurity may be inappreciable, being so infinitesimal.

tesimal that no balance yet constructed can show them. Though a balance may be inoperative, yet, as is well known, light is able to show us impurities in a substance which may not be one-millionth part of a grain in weight. By passing the light emitted from heated vapours of the substance and its impurity through a prism, and noting its spectrum, we may be able to detect the latter.

The spectroscope will not tell us at present, however, whether the silver or potassium is present as nitrate, chloride, bromide, oxide, &c.

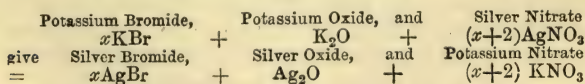
Where we are dealing with silver salts which are sensitive to light, and which are amenable to development, it is possible to ascertain whether certain compounds of silver are present. Impurities in the bromides, with which the silver bromide, for instance, is to be formed, can, in some cases, be shown by weighing. For, in a paper read before the Photographic Society of Great Britain on the 8th of February, 1876, Mr. Warnerke stated that on testing the different bromides, he found that considerable variation from the theoretical quantities necessary to combine with silver nitrate was observable.

Potassium bromide is one of the most usual salts with which to form silver bromide. Let us see how it may be contaminated in its preparation. We find that the mother liquor from the sea water brine is treated with chlorine, and that this takes the place of the bromine which in sea water is in combination with magnesium; the yellow liquid is agitated with ether, which takes up the bromine, and this ethereal solution is treated with potash in solution. The bromine forms the bromate and bromide of the alkali, and when the alkali is nearly saturated, it is decanted off and further treated. Now, from what we have said before, it is more than probable that the bromide is contaminated with the alkali, however well it may be separated: the traces of alkali may even be so small as to be undetected by litmus paper.

Again, the bromides of the alkaline metals are prepared by acting on the alkalies with an excess of bromine, a similar reaction to that above taking place. The bromate is decomposed by ignition, and this heating alone tends to decompose the bromide, in which case we should have the oxide of the alkali left behind. In good preparations it would be excessively small, but still sufficient for the purpose we shall indicate presently.

The bromides of the metals may be similarly contaminated. Take zinc as an example; the metal is easily oxidized, and the zinc oxide is soluble in zinc bromide, as it is in the chloride. In all these cases, then, it is possible we may have traces of oxide with the bromide. Again, there are some metals which form two bromides, as that of copper; and experience shows that it is very hard to get all compounds fully saturated with bromine, a part of it being generally in the less saturated state.

If such bromides, contaminated with the oxide, or containing the lower combination of bromine, be brought in contact with silver nitrate, we shall have two separate reactions to consider. In the case of the oxide contamination, when silver nitrate is in excess, we shall have—



Or, besides the silver bromide, we shall have silver oxide formed.

We have seen that we may have oxides and sub-bromides contaminating the bromides, and in a similar way we may have oxides and sub-chlorides contaminating the chloride. The writer has shown that it was possible to develop an image on a film never exposed to light, but which was in contact with a film (during the operation of development) on which an invisible image had been impressed. The explanation offered seems in every way to meet the requirements of the case, which is, that where

a nucleus, if it may be so termed, exists, there the silver from the adjacent bromide during development will be deposited in preference to any other part of the film. Such a nucleus is found in the silver sub-bromide or sub-chloride when the one film is exposed to light. If it be chemically produced, we may assume it will act in a similar manner.

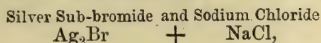
The case of the oxide is not so clear; but a little experiment will throw light on it. Prepare silver oxide as an emulsion in collodion; dissolve (say) 6 grains of silver nitrate in an ounce of plain collodion, and add to it two grains of potash in alcohol. This will give an emulsion of oxide of silver. Now wash it, and add a drachm of it to an ounce of a washed collodion emulsion which works perfectly free from fog; coat a plate, and develop it. It will be found that a veiled image is produced. In this case the silver oxide (presumably partially reduced to the metallic state, since the oxide is an unstable compound) acts as the nucleus on which the silver bromide is reduced to the metallic state by the alkaline developer.

It must be borne in mind that the invisible image must necessarily be composed of very minute particles of the altered silver salt. If, then, such a small number of such particles distributed over a film are sufficiently powerful to form nuclei for the development of the image, the same minute quantity of oxide, or chemically-produced subhaloid of silver, might be capable of producing the same results. The above, then, seems to be the explanation of fog in emulsion plates. Now as to the remedies.

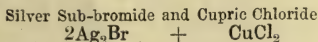
It is well known that when we have an excess of soluble haloid, freedom from fog is secured. In some experiments we carried out, we found that silver bromide is formed before any other silver compound, except the iodide, when the sensitive salt is formed from haloid salts, and not from the halogens themselves. Thus, if potassium bromide be contaminated with potash, we shall have both silver bromide and silver oxide formed, if an excess

of silver nitrate be added ; but if there be a defect of the nitrate, there will not be a trace of silver oxide, but only silver bromide. Again, if we take bromide of copper, which is usually contaminated with the sub-bromide, as already stated, it will be found that the bromide is all utilized before the sub-bromide is attacked at all ; and if, in addition to the bromide, we have a metallic chloride present, which may be contaminated with sub-chloride, the order in which they will combine with the silver nitrate is : bromide, chloride, sub-bromide, sub-chloride. Thus, if there be only sufficient silver nitrate added to an emulsion to combine with the two first on the list, the other two will be left in the emulsion as harmless compounds. The method of eliminating fog from the finished emulsion in which there is *at first* an excess of silver nitrate is thus easy to guess, and we have the theoretical explanation of a statement made some years ago by Major Russell, that a little soluble bromide ought to be left in the film when silver bromide is formed by the bath in the usual way. It may be remarked, parenthetically, that whether the image be developed by the alkaline or acid method, the same result must hold good. Supposing we have a *washed* emulsion which contains bromide, sub-bromide, and oxide of silver, and also a very slight excess of silver nitrate. The addition of certain metallic chlorides or of hydrochloric acid will at once convert the sub-bromide and oxide into the chloride of silver, leaving harmless compounds behind. The metallic chlorides which are of use are those which readily part with chlorine, and which, therefore, preferably form more than one chloride, such as gold, copper, platinum, &c. When other chlorides, such as of the alkalies, are employed, the needful substitution may not take place, because the affinity of the alkali for the chlorine is greater than for the sub-bromide ; and therefore the elimination of the sub-bromide is not effected. Thus, if all the silver nitrate in original excess be converted into silver chloride, we have the silver sub-

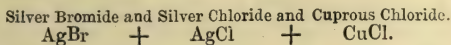
bromide to get rid of. Now, supposing we are using sodium chloride as a corrective, then we should have



which can form no new saturated silver compound, since an atom of metallic silver, sodium, bromine, or chlorine, cannot be left in a free state; but if we use (say) copper chloride, we have—



which can form—



The CuCl , or sub-chloride of copper, is harmless, and can be left out of consideration.

It will, therefore, be seen how it is that addition of these chlorides to a washed emulsion will give freedom from fog.

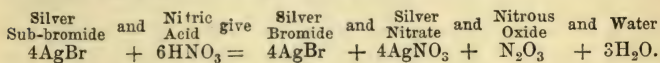
Secondly, if an excess of silver nitrate be used, it is evident that something else besides a mere chloride will be required, since the sub-salts and oxides would be formed. This we find in the employment of an acid, or of a halogen itself, or both together, added to the emulsion, to be most rapidly effective. Whatever is used is best added to the soluble salts before the silver nitrate is added.

Suppose nitric acid alone be employed, then any oxide or carbonate will immediately be attacked, as also any of the sub-bromides—such as of copper. Again, if aqua-regia be employed, we know that chlorine is evolved in an extremely nascent state, and that this would attack either oxide or sub-bromide, fully saturating the unsatisfied atom in the latter. If, now, silver nitrate be added, silver bromide and chloride would result with some compounds (perhaps such as the chlorate), which would be as inert as producers of fog as the silver nitrate itself.

If a halogen be employed without any acid, the same result would occur. Thus, suppose we had as impurities

an oxide and a sub-bromide, and that we added a solution of bromine to it, we should get the oxide changed to a bromide and bromate (the latter salt of which is experimentally proved to be inert), and sub-bromide changed to a bromide.

If the halogen be added last, when there is an excess of silver, it is probable that until all the latter is converted it will exert no unfogging action; but if an acid, such as nitric acid, be added, it will exert its proper influence, though slowly; for it will convert any oxide or compounds of the oxide into nitrate, and from the silver sub-bromide dissolve away the loose atom of silver, converting the sub-bromide into bromide and nitrate. Thus—



Or, at all events, a fresh combination will be made, which is unacted upon by the developer.

There is also a method of eliminating fog from collodion dry plates when coated, without doctoring the emulsion at all. This need not apply only to washed emulsions, but it can be effected during the washing of the plates prepared by the unwashed emulsion. In addition to the elimination by the acids, and by the metals forming two bromides or chlorides, we can further effect it by using a solution of potassium bichromate,* permanganate of potash, or peroxide of hydrogen, and other oxidizing agents, such as ferric-sulphate and ferric-oxalate. The reason of this seems to be due to oxidation, or to the direct formation of a new product; the writer is still engaged in experiments on the subject. It may be, in the first case, that a minute quantity of silver bichromate is formed by the oxide, or that the free silver atom of the sub-bromide is oxidized, and then formed into silver bichromate; with the second, it may be that the man-

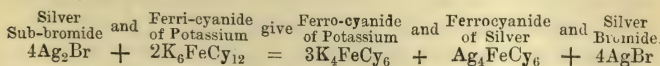
* This can be used with gelatine emulsions.

ganese salt is substituted for the silver salt, and is inert ; and in the next two cases it may be that the silver salt is per-oxidized, and forms an oxy-bromide, which is unaffected by the developer. This seems probable, since ozone has the same effect on the fog.

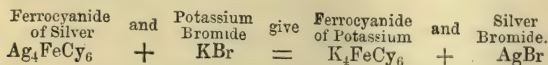
It may not be uninteresting to note an experiment which throws some light upon this point, though it is not conclusive. If a plate be coated with collodion emulsion, and be allowed to thoroughly darken in the daylight, and then drops of the above oxidizing agent be placed on different parts of the film, and allowed to act for a few minutes, it will be found, after washing, that on these spots the colour and appearance of the film will remain unaltered. (Where the manganese has been, the film is slightly brown.) Now, if the film be treated with sodium hyposulphite, the parts where all have been will become transparent, showing that everything except the collodion has been dissolved away, whilst on the rest of the plate there will remain a delicate layer of metallic silver. This shows that the loose atom of metallic silver attached to the sub-bromide has been converted into a salt soluble in hyposulphite of sodium.

Be the theory what it may, the treatment holds good. Perhaps with collodion plates the application of nitric acid is the safest, where possible, but to that we shall refer later on.

Dr. Eder has also shown that potassium ferri-cyanide and potassium bromide will cause the same result. The ferri-cyanide acts as follows :—



The potassium bromide converts the ferro-cyanide of silver into bromide, and ferro-cyanide of potassium is formed. Thus—



From the foregoing it will be seen that fog may be produced by inorganic matter present with the silver salt; and further on it will be seen that it may be produced during development and in emulsification. Regarding this last point there is more to be said in regard to gelatine emulsion, and which will be found more fully treated of later on. Suffice it to say that gelatine itself, when decomposed to any extent, has an alkaline reaction, ammonia being one of the products, and that this will reduce the silver bromide held in suspension in it, unless means be taken to overcome the effect of the alkalinity, or to neutralize the alkalinity. In other words, decomposing gelatine is a feeble developer (or reducer of the silver salt), and may cause fog. The fog caused by the reduction of the bromide to the metallic state is much more difficult to treat than any other, for the mere conversion of the metallic silver into oxide is useless (see page 24). More vigorous treatment is required. This shows that a collodion emulsion is much more readily unfogged than a gelatine one, since in the former the reduction of the silver salt to the metallic state rarely, if ever, occurs. With collodion the danger is minimized, and acidity rather than alkalinity is to be apprehended.

With gelatine plates it is inadmissible to use any substance which may attack the gelatine; thus the application of acids is not to be thought of, nor hydroxyl, nor permanganate of potash. Chloride of copper may be employed, but the safest plan is to use either bichromate of potash or the ferri-cyanide of potassium with the bromide of potassium.

CHAPTER IV.

DARK-ROOM AND ITS FITTINGS.

It is of course convenient to have a special dark-room adapted for all photographic work, but in some cases it is impossible, we are well aware. If, however, the amateur will work after dark, there is no reason why a dressing room, a bath room, or any spare room should not answer the purpose without permanently disarranging them. For the preparation of emulsion and plates the requirements are of course greater than when merely development is to be carried on. For the latter, a wash-hand stand and basin, five or six dishes, a drying rack, and a piece of mackintosh (to prevent spoiling the furniture or carpet by any splash from the developer), are sufficient for any purpose, always provided the light used in illuminating is made subservient to the purpose for which it is to be employed. In making collodion emulsions, any ordinary room will answer; and plates may be prepared if a drying cupboard of some description or other is provided. For the manufacture of gelatine emulsions, much may also be done, only in this case it is necessary to have some convenient gas-stove for heating them, and hot water as well. One of Fletcher's numerous burners may be employed with every satisfaction in the majority of cases, and it need not be a permanence in the room, since it can be attached to any

gas jet. The following description of a dark-room is taken from "Instruction in Photography."

The size of the dark-room may, of course, vary, but it may be remarked that a place six feet square is the least space in which to work.

A sample of an arrangement for such a size of room is given in the figure. B is the sink ; AA are the two work-

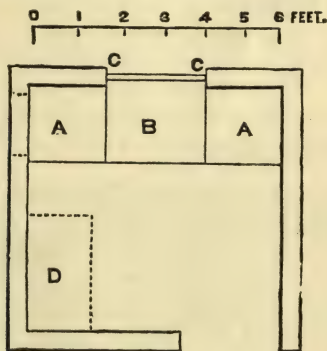


Fig. 3.

ing tables. On the left, over A, may be placed a glass shelf, running along the left wall towards the drying cupboard, D. The right hand table, A, may be used for the developing bottles and apparatus. The door of the dark-room should open outwards, if possible, and be covered by a curtain, which depends on to the ground, thus shutting out all light which would otherwise get through the chink between the door and the floor. Too many precautions to exclude white light cannot be taken, since gelatino-bromide, if it is to take the place of collodion, should be extremely sensitive to it, however feeble it may be.

Water Arrangements.—It is always useful to have water laid on to a dark room, but in many cases it is impossible ; in that case we recommend that a two-gallon jar be placed some three feet about A (fig.) on the right hand, a hole

being bored about two inches from the bottom. A cork with a pierced hole, in which is passed a small piece of glass tubing, should fill up this orifice, and on the glass tube should be drawn a piece of black india-rubber tubing of a convenient length, to which an American clip should be attached. If a hole be bored slantingly through the clip, so that the india-rubber tube, when passed through it, comes to the termination of the jaws of the clip, this arrangement, which was first described to us by Mr. England, will answer better than more elaborate contrivances. When water is laid on from the main, a rose is a very desirable adjunct to the tap, since it gives a jet which has no force, and which is like a shower or spray.

Drying-Cupboards.—The principles on which a drying-box should be made should be apparent, though in many forms they are neglected. The first principle which should be carried out is that the air passing through it should be capable of taking up moisture. It very often happens that the air which, in some contrivances, is passed through the drying-box is nearly saturated with moisture, hence it can take up but very little more, and plates dry slowly. Air, of course, may be dried by causing it to bubble through sulphuric acid, or by passing it over dry chloride of calcium; but in order for this to be effective, the drying-box must not only be light-tight, but also fairly air-tight, since the air would find its way immediately through any small chink or cranny sooner than force its way through these obstructions. A better mode is to warm the air entering the box, so as to cause a draught, and at the same time this slightly warmed air will hold more moisture than cooler air. On this principle sound efficient drying-boxes are constructed.

An excellent type is that due to Mr. England. If constructed as in fig. 4 it will dry plates up to 12 by 10.

A box is made of the dimensions given, and one side is hinged, and opens as shown. This side has a fillet

placed round it, so that on shutting up no light can enter the interior of the box. Through the centre of the box runs a gas pipe, at the bottom of which is inserted a

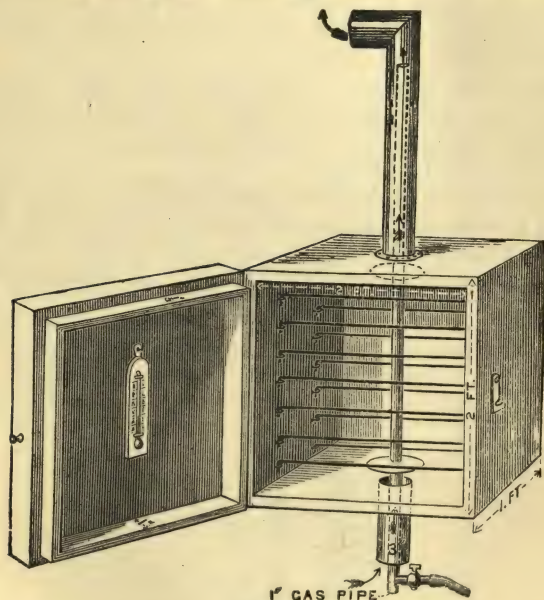


Fig 4.

small tube closed at the end, and on one side of which is pierced a small hole. To this hole gas is led, and a very small jet is lighted in the gas pipe. At the bottom of the box, and at the top, are two holes of about three to four inches diameter; and above, two tin tubes, some twelve inches long, are fitted into these tubes as shown in the diagram. It will be noticed that the gas piping passes through the centre of these two tubes. Round the gas pipes are fitted two discs of blackened card or tin, one of which is placed two inches above the bottom hole, and the

other the same distance from the top hole. These prevent light striking down the tin tube into the box. The plates, when set, are laid on pairs of wires stretched across the box, as shown in the diagram, and a box of the above dimensions may take from half to one dozen plates on each side of the central pipe.

Plates dried in such a drying-box are ready for use in about twelve hours after coating. A small thermometer should be hung on the cupboard door, to enable the temperature to be noted.

The rationale of this fairly rapid drying is that the gas piping gets heated, warms the air in contact with it, which ascends through the top tin tube, and a current of fresh air comes up through the bottom one. A constant change

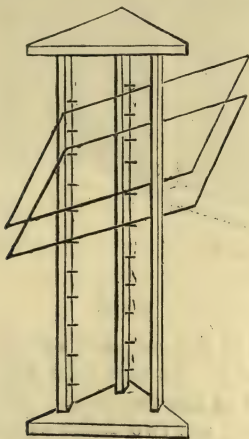


Fig. 5.

of air, more than a very dry or hot air, is the object to be attained.

We are in duty bound not only to give its excellencies, but also to point out any defects. In hot weather we found that the parts of the plates dried close to the central pipe

are apt to run; the heat is communicated to the iron wires, and the glass takes it up, and the gelatine is apt to melt when the plate touches the wires. This is evidently due to conduction, and we believe that it is better to have a non-conducting medium in contact with the glass. Small loose cylinders, about half-an-inch long, of pipe-clay, can be readily baked and slipped over the iron bars, and each end of the plate supported by them. For summer weather, when the air is, as a rule, dry, it is a good plan to have a small gas jet placed just above the box in the iron gas tube. This heats the air in the zinc tube, and a draught is created through the box; by this means the air is not above the summer temperature, and is not so quick drying. For our own part, when drying gelatine plates, we use racks similar to that shown in fig. 5. A cupboard will dry nearly double as many plates on these racks as when they are laid to dry horizontally. Collodion plates may also be dried in these racks.

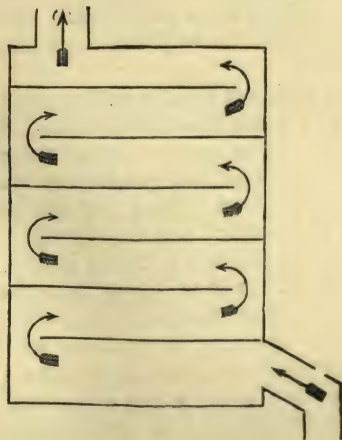


Fig. 6.

The plan recommended by Dr. Van Monckhoven is one

which has long been in use in England, but he has described it as follows:—"The drying-box (fig. 6) is easily made, and consists of a box of thick wood, on the top of which is a zinc pipe to connect it with a chimney. At the bottom is another pipe, but with an elbow to prevent light from entering. Horizontal shelves are placed in the interior, so that the current of air obtained by the draught in the chimney goes over each, one after the other. This box ought to be placed in a warm and very dark room. As to the necessity of warmth in the room, we demur. It is not necessary if arrangements be made for burning a gas jet in the top tube, so as to create a draught."

Mr. A. Cowan has also described in the Photographic Almanac a drying box for dry plates which is essentially correct in principle, and no doubt answers well. He says:

"It often happens in very damp weather that gelatine negatives refuse to dry for hours, and even when flooded with spirit take a considerable time.

"To those who do not possess a good drying cupboard the following is offered as a thoroughly efficient substitute, which anyone can make for himself with a little help from the blacksmith.

"The annexed diagram (fig. 7) will explain itself. The box may be of any form most convenient, but the more shallow the better. The one in actual use stands on an ordinary work-bench, and the gas-burner, and iron cone, &c., on the floor, enclosed with a few bricks piled up to keep in the heat and protect any woodwork. A very good proportion for the cupboard is thirty inches high, thirty inches wide, and ten inches deep from back to front. The front is closed up at the lower part about six inches, and a sliding door running in grooves closes the upper part all but about half an inch from the top, a balance weight over a pulley supporting it in any position required. This is found a much better way than having doors opening on hinges, for various reasons.

"The current of warm air is conveyed in at the bottom

through a three-inch circular opening, the iron stove-pipe arrangement being screwed on underneath. Above the opening, at a little distance, is supported a thin shelf of wood about an inch smaller all round than the inside of the

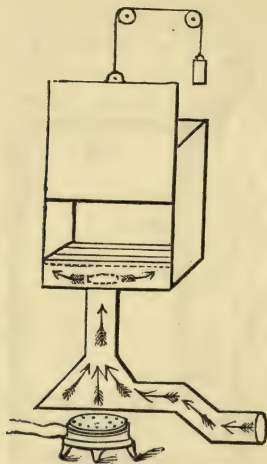


Fig. 7.

box, which acts as a diffuser, and stops the current of hot air from rushing up in one spot. Above this, at any convenient height, two bars are fixed to carry the feet of the drying rack containing the plates. It will be found that plates will dry without running at a very considerably higher temperature than that at which gelatine melts if the heated air be kept in continual motion."

Another excellent drying box, due to Mr. Rogers, is shown in fig. 8.

The section of the box shows the general principles adopted; the exit pipe for the warmed air is at the top of the box. The drying-box may be of any dimensions. P is a one-inch piece of gas-piping standing on the box C, and through it a small pipe, carrying a minute gas-nipple,

passes; it is soldered in air-tight at the bottom of C, and is connected by an india-rubber tube, I, with the gas; Z is a three-inch stove-pipe, soldered up at one end, and open at the other, through which P passes; a small leather washer, W, makes the zinc-tube air-tight at the top; D

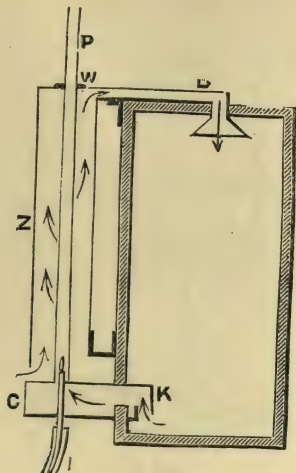


Fig. 8.

is an outlet tube passing into the top of the box, over the opening of which may be stretched muslin in order to arrest the entrance of all dirt into the interior. At K is a light-trap, to exclude all light which might be reflected from G, the gas jet; a current of warmed air thus perpetually circulates in the box B. The gas is lighted by raising the pipe P from off C, which is then replaced. In summer the tube D may be closed, and an inlet pipe, coming from the top of the box, be substituted for it, thus causing only a current of air at the ordinary temperature of the room to pass through it. We may mention that the plates dry more rapidly at the top of this box

than at the bottom. This is due to the warmer air having a tendency to remain at the top.

Another excellent plan for a drying cupboard is the following, which has been devised by the writer.

B is a zinc boiler, from which are taken two pipes, D and H, leading to the coil of pipes, C C C C. A supply tank, T, is fastened against the side of the cupboard, and a supply pipe joins the coil pipe at H. From D another pipe, A, is led, terminated with a tap, which allows any air to be got rid of, which would otherwise stop the flow

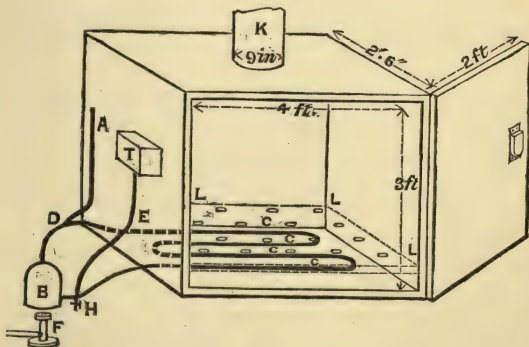


Fig. 9.

into C C. At H is a tap, which allows the whole apparatus to be emptied at pleasure. K is a hot-air shaft, being some four feet above the box. It is terminated by a bend in two directions, and can be fitted with a cap, if required, in which are pierced orifices. Beneath are a couple of ventilating inlet pipes, likewise bent in two directions. L L L is a false bottom, pierced with holes, on which the drying racks are placed. F is a gas jet, which heats the water. (The cupboard is shown with only one door.) Each door is made light-tight by means of fillets, which need not be described. The hinges are

pianoforte hinges. The piping is made of composition gas-pipe, though perhaps iron would be better; still, as they are, they answer perfectly.

In this cupboard it is well to have the plates on horizontal racks, so that the warm air may pass rapidly over them.

CHAPTER V.

ILLUMINATION OF THE DARK ROOM.

IN all emulsion processes, whether collodion or gelatine, great precautions have to be taken as to the light in which the plates are prepared, since they are necessarily exposed to its action for some considerable time. There are many persons who attempt to prepare emulsions who fail, and the failure may often be traced to the improper lighting of the dark-room. For development, a light which would slightly fog a plate during preparation may be used, since it is not necessary that it should be exposed to its action more than a second or two, which would not be sufficient exposure to cause any perceptible fog. When once development begins, the ingress of more actinic light has but little effect, since there is sufficient bromide used in the development, with the alkaline development, to render the silver salt insensitive or, if ferrous-oxalate be employed, the solution itself is of a colour which effectually cuts off all light that would rapidly harm the image. We have made these remarks, not to discourage the idea that a perfectly safe light should be used, but to show that when such cannot be procured, as on tour, it is possible to develop plates without any danger. It is necessary, first of all, to know what kind of plates are to be prepared,

and worked, before deciding what light to admit to the dark room. For instance, with collodio-bromide, an orange or yellow light will suffice; but with gelatine plates containing pure bromide, a ruddy light in which there is but little green is the safest. It is safe, however, in all cases, to have a red light of the right kind, and we recommend it for general adoption, since every kind of plate can be worked in it.

If the quality of the light can be got by which the salt of silver is unaffected, the quantity may be unlimited. To make this more clear, a diagram from another work* is reproduced, from which, together with a reference to figure 2, page 4, a notion can be obtained as to the light to which different plates are sensitive, and the media which may be accepted to cut off that light.

No. 1 may be omitted from consideration, since it is sensitive to all rays, and no filtered daylight is admissible where it is employed; but Nos. 2, 3, and 4 should be studied. When a streak of white light is passed through a prism it is spread out into its component colours, and in 14 they are represented as white. The black portions in 2, 3, and 4 of the diagram show the rays of light in every case which do not appreciably affect a sensitive plate. The white and half-tints represent, as approximately as can be shown in a wood-cut, the relative sensitiveness of the plates, the different rays forming white light; the degree of sensitiveness being indicated by the degree of whiteness. It will be noticed that the gelatino-bromide and collodio-bromide plates are sensitive to the confines of the red, and some specimens of the former are also sensitive well into the red, whilst the bromo-iodide here shown is only sensitive to the confines of the yellow. Next we need only turn our attention to Nos. 5, 6, 7, 8, 9, 10, and 12. In these are shown the rays of light which pass through different coloured glasses and dyes.

* "Instruction in Photography" (Piper and Carter), 6th edition.

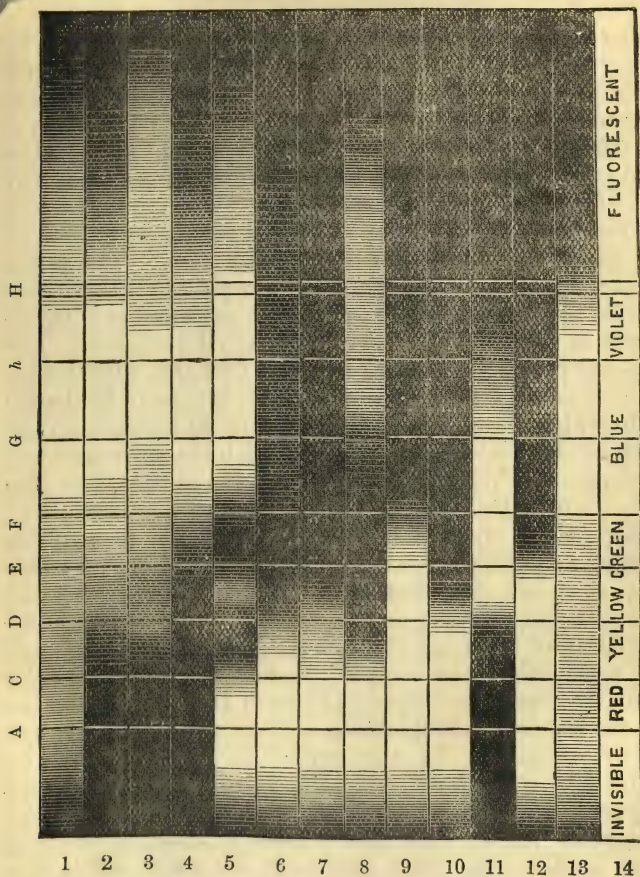


Fig. 10.

1. Special collodio-bromide.
2. Gelatino-bromide.
3. Collodio-bromide.
4. Bromo-iodide.
5. Cobalt glass.
6. Ruby glass.

7. Chrysoidine.
8. Magenta.
9. Flashed orange.
10. Stained red glass.
11. Bottle-green glass.
12. Aurine.

13. Quinine.

Ruby glass would be as near perfection as possible for every plate were it not that a certain amount of blue light passes through one thickness of it. When two thicknesses are used the blue is imperceptible. By the use of a combination, orange glass and ruby, or stained red glass and ruby, the light allowed to pass through is such as will not affect most plates unless the exposure to it be prolonged, since the orange or stained red entirely cuts off the blue which may permeate the ruby glass. The writer has been told that some people prepare plates so sensitive to the red that the light passing through any number of thicknesses of ruby glass proves an ineffectual protection. Unless ruby glass were added till total darkness supervened, there is nothing to surprise us in this statement, as the red light which filters through three or four thicknesses of ruby glass has the same quality as that which filters through two thicknesses. What they really express is that they prepare plates which are in reality sensitive to red light. When this is the case the development and preparation of such an emulsion become a nuisance, and are probably more of a scientific than of a practical value, since the same sensitiveness can be produced without any liability to veiling of the image through the impact of light of such low refrangibility on the plate. For an ordinary dark room we recommend that, if a north light be obtainable for the window, one thickness of ruby and one of stained red or orange glass be employed. As to dyes, it will be seen that if glass be coated with aurine on one side, and magenta on the other, the same spectral quality will be obtained. At the same time it must be remembered that every aniline dye fades gradually in white light, the fading being caused by those rays which they absorb. Under these circumstances, if orange glass be placed outside the paper dyed with the foregoing, the means of obtaining a room permanently lighted with a safe light is increased. If plates very sensitive to the red be prepared, one thickness of cobalt glass and one of stained red

will be the best combination to use ; but, as we said before, plates requiring such a light by which to develop should not find a place in a photographer's hands. If the sun shine on the window during any part of the day it is well to have a screen, which can be placed against the window-frame (it can be hinged from the top, and pulled up as a flap by a small pulley arrangement), covered with orange-coloured paper.* This diffuses the light, and renders any chemically active rays which can possibly filter through it less hurtful. It is not always practicable, however, to work by day, and then it becomes necessary to resort to artificial light, and that must be of the same character as the filtered daylight. Now, candle and gas-light have not the same amount of blue in them as the light from the sun, hence the screen used for shielding such sources need not be quite so perfect. In our practice we have a lantern made like a large sized stable lantern. Holes are pierced at the bottom of it for the indraught of air, and holes at the top of the sides for the outdraught. To prevent any light striking the ceiling, we have had a tin cover fitting round the lantern† at the top, and sloping 45° downwards, by which means any light glancing through the holes strikes the shade and is reflected downwards. The sides are covered with two thicknesses of orange paper, and a candle placed inside gives a very fair working light for coating plates or for development. As may be inferred from our previous remarks, the light must be much more subdued for the former than for the latter purpose. There is a medium called canary medium which has lately been revived for use in the developing and coating room. It is a paper which is impregnated with chromate of lead, and we have tested its capacity for cutting off hurtful light. For most plates it answers well when two thicknesses are employed, but it is inferior in illumination

* Common orange packing paper answers admirably.

† Some lanterns are made with this arrangement.

to the orange paper. It is a pleasant light, however, to work in, and it is to be recommended. Before packing plates, it is always necessary to examine them for dull spots and imperfections. As a rule, the diffused light coming through paper or other fabric is unsuited for this examination. It is better for this purpose to have a lantern with a transparent side, by which means the flame of the light is reflected from the plate to be examined, and this immediately throws in view any imperfections. As the examination can be made in a couple of seconds, this exposure does not injure the plate.

Some dry-plate men we know have gas burning close outside a red glazed window which opens into an adjoining room, but it is not every one who can have such an arrangement.

For developing plates at night, whilst on tour, we have

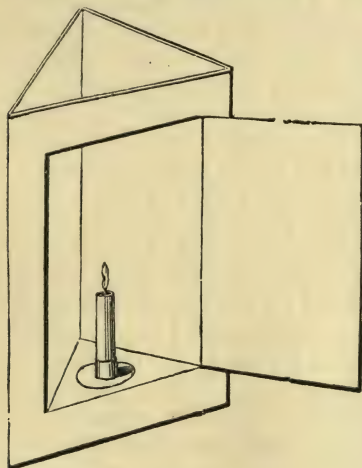


Fig. 11.

found that a useful piece of apparatus can be easily made. Take a sheet of cardboard of the size of about 2 feet by

1 foot 6 inches. Lay off from the 2 feet side distances of 8 inches from each corner, and with a penknife cut half through the card in a line parallel to the ends. These will form flaps, which can be folded over to meet in the centre. From the centre portion mark out a rectangle of about 6 inches by 12; cut round three of the sides, but only half cut through one side, the penknife being applied from inside of screen. This will allow a square flap to open outwards. On the inside of the opening may be pasted or hung a sheet of orange paper; or a sheet of paper dyed deeply with a mixture of aurine and aniline scarlet may be glued to it. The candle is placed behind the screen, which should stand, supported by the two wings, in front of the operator. A piece of board, or a piece of tin, may rest on the screen, and thus cut off diffused light from the ceiling. We have developed many plates with such a light, and lost none by veiling of the image. When packed for travelling, the flaps are folded up, and it can be placed in the portmanteau.

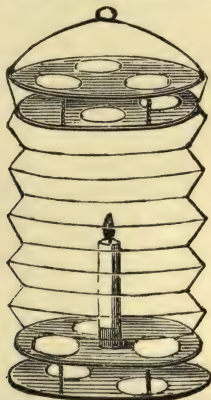


Fig. 12.

A useful portable lantern is made from a Chinese lantern. We first saw it adapted in Mr. Galton's hand; but

Dr. Hermann Fol has given a practical method of its construction in the *Photographic News*. He describes it as follows:—"The most portable lantern I make by painting over common white paper Chinese lanterns with collodion containing castor oil and fuchsine. The top and bottom of the lantern are made each of two thin metal plates fastened together by three small chains. Each plate is pierced with holes, and each pair is fastened to the chains so that the holes do not correspond, and half-an-inch remains between the two plates. No white light can then find its way out. The upper pair is, of course, unfixed, and may be lifted out to get access to the candle. This lantern folds up into the smallest possible compass, and when in use perfectly excludes all actinic light without getting hot."

Dealers supply lanterns more or less efficient, but we confess to liking home-made apparatus, since, if made by oneself, they can generally be readily repaired.

CHAPTER VI.

INTRODUCTORY REMARKS ON GELATINE EMULSIONS.

Historical Outline of the Process.—A gelatine emulsion, as it is somewhat crudely called, as first made by Dr. Maddox in 1871, is in reality silver bromide, &c., emulsified in a gelatine solution, with which plates are coated. We have already (page 3) stated that there are various modifications of the molecular state of the bromide, which are brought about in a variety of ways. Mr. C. Bennett first showed how extremely sensitive plates could be prepared by keeping the gelatine solution liquid at a temperature of about 90° for six or seven days. What he accomplished was in reality to bring about a modification which was very easily acted upon by light. It need scarcely be said that in certain states of the weather this long emulsification was attended with enormous risks of decomposing the gelatine, and when gelatine decomposes, the products are apt to reduce the silver bromide to the metallic state, and hence to cause fog. Besides this, there is the danger, even if fog is not produced, of the gelatine refusing to set. Col. Wortley stated that he got the same rapidity in his plates by raising the temperature of the emulsion for a few hours to 150° F., and Mr. Mansfield first recommended the gelatine

emulsion to be brought to the boiling point; but then a very short boiling is liable to destroy the setting qualities of the gelatine. Mr. W. B. Bolton, in an article in the *British Journal of Photography*, first indicated the true method of preparing emulsions by boiling. He emulsified in a small quantity of gelatine, boiled, and then added to the emulsion the proper quantity of gelatine to give it a firm consistency when setting. We may say that the publication of this article opened out a new era in gelatine emulsions. We need not further explain the *rationale* of the process here. Dr. Van Monckhoven called attention to the fact that by adding ammonia to the silver bromide, a modification was obtained which gave great rapidity; and Dr. Eder carried the principle further, and gave a really workable, though in some states of weather a dangerous, process. The great *desideratum*, according to these authorities, was to obtain a grey emulsion by transmitted light, and green by reflected; but, as will be seen from our remarks on page 3, this state is not what we consider the most sensitive, and certainly we have never obtained plates so rapid by the ammonia process as we have by the boiling process. We have endeavoured in the following pages to give an accurate description of the way to carry out all these processes. But we here make a distinct record of our opinion, which is, that for rapidity and good quality, the boiling or hot digestion processes are the best and safest.

We have also given processes for precipitating silver bromide in water or glycerine and water, and then adding it to gelatine. The processes are effective, but they are not so easily employed where iodide is used, as the iodide is apt to settle down in large particles.

We here give one piece of advice, which is, that if the reader has a process with which he is thoroughly satisfied, he should keep to it, and not waste his time or energy in following out more elaborate, but perhaps less successful, processes.

A pertinent question for everyone to ask himself is, as to whether a very rapid process is always a *desideratum*. For our own part we unhesitatingly say it is not. For transient effects in a landscape, for instantaneous views, or for portraiture in dull weather, rapid plates are useful adjuncts, but should be nothing more. We believe that finer pictures, more mellow and truthful, are usually produced by the slower plates, be they collodion or gelatine.

On the Causes of Sensitiveness in Gelatine Emulsion.—It may be said that in a gelatine emulsion it is almost necessary that the soluble bromide be in excess over the silver nitrate; that is, that when all the nitrate is converted into bromide, there should still be soluble bromide left in the solution. It must be recollected that gelatine is a most unstable body, and we believe we are correct in saying that from the first time it is heated its decomposition commences. This decomposition at first gives rise to an acid reaction, and eventually to an alkaline one. In the first stage no harm will ensue to silver bromide suspended in it; but when the latter stage is arrived at, there is a great tendency for the silver salt to be reduced to the metallic state, unless some body be present which hinders it. Such bodies are found in acids and soluble bromide. The addition of acid must be made cautiously, since acids cause gelatine to lose its setting properties, and there is, consequently, a greater safety in using excess of bromide. Again, if there were any excess of silver nitrate, this excess would combine with the gelatine, and we should have a product formed not particularly sensitive to light, but acted upon by a developer at once, and have in consequence a production of red fog. We may, therefore, take it that in the production of gelatine emulsion an excess of soluble bromide is essential.

In the first chapter we have already referred to the differences in molecular structure that silver bromide may assume; and we repeat that the molecular structure

is purely due to physical causes, and *not* to different chemical composition; in other words, bromide, chloride, and iodide of silver emulsions have always the same proportions of bromine, chlorine, and iodine to silver present.

When silver bromide is produced with proper precautions as an emulsion, or in the film at once, as in the wet collodion process, we have the film transmitting red rays, and absorbing the blue rays; showing that the work performed in the film is really done by the blue rays. If a gelatine emulsion, however, be boiled, the bromide, unless great care be taken in mixing, becomes a cold grey colour by transmitted light, and yellowish-green by reflected light, and this shows that some of the yellow and red rays are absorbed, whilst some of the blue rays are transmitted; and yet it is found that this silver bromide is more sensitive to the blue rays than the redder form. Can any explanation be given of this? We think it can. It is not owing to the fact that the silver salt is slightly sensitive to the yellow rays, for this would only increase the sensitiveness by about one-twentieth, as photographing the spectrum shows us. It must be recollected that the apparent colour of the bromide may be produced in two ways—or rather, that it may be due to two causes: it may be due to the colour of the silver bromide itself, which is what we may call its molecular colour, or a variation in colour may be due to the scattering of light by the different sizes of the particles, each particle being probably composed of thousands of molecules. When an emulsion is boiled, an inspection of the films after different lengths of boiling will convince us that the longer an emulsion is boiled, the larger the size of the particles which are embedded in the gelatine. Hence boiling produces large particles. The cause is, probably, that silver bromide is slightly soluble in water, *and much more so* in water containing soluble bromide. Without doubt, during boiling some portions of the silver bromide are dissolved and re-precipitated on the coarser particles, other por-

tions of the finer bromide being taken up, and they in their turn deposited, and so on.

Mr. Wilson, in his description of his gelatine process (which won the Paget prize), and which statement we overlooked when we subsequently experimented in the same direction, says:—

“The proportions of soluble bromide and silver nitrate are very important. Contrary to usual statements, the larger the excess of silver bromide, the more quickly is the AgBr converted; if there be but little excess, a very long cooking will be required; and if exactly the equivalent quantities could be used, the writer believes that no amount of cooking would give the sensitive condition. Too large an excess, on the contrary, tends to form fog, which is not to be afterwards got rid of by the use of bichromate, but which is more liable to occur with alkaline pyrogallie developer than with ferrous-oxalate.”

Practically we have proved that by increasing the proportion of soluble bromide to silver nitrate, up to a certain point, a great increase of sensitiveness is brought about.

Now, we have shown (page 18) that metallic silver cannot exist in contact with silver bromide, but that the latter becomes at once amenable to development by its conversion into sub-bromide. Suppose, then, that one molecule of one of these particles is affected by light, the rest of the particle would be reduced and give the appearance of increased sensitiveness, since sensitiveness is only recognized by a visible quantity of metallic silver. Thus, if the particles in one were only one-tenth part of the size they are in another, it is quite within the range of probability that the sensitiveness of the former might be concluded to be only one-tenth of the latter, whereas the light might have done precisely the same work on the two.

It might be supposed that a perfectly neutral state, or an alkaline state of the emulsion, should be conducive to sensitiveness, and seeing the use made of ammonia, there

is, at first sight, much in it. Dr. Vogel, however, has, by the production of an acid emulsion (which he classes as sensitive as ordinary gelatine plates), proved that such is not the case. The production of this emulsion, one solvent of which is acetic acid, and in which silver bromide is not soluble, is most valuable in a theoretical point of view (always supposing that no material loss of sensitiveness is produced by it) being one more proof that the sensitiveness is due wholly to a physical change, and not to a chemical change, in the silver bromide.

There is another fact of especial interest, which is, that keeping an emulsion after preparation previous to coating the plate is conducive to sensitiveness. The following table will show the increase given by keeping. The increase is gauged by taking the first day's sensitiveness as unity. The emulsions were washed, and melted, and a small portion taken out of the jelly each day.

| | 1st day. | 2nd day. | 3rd day. |
|----------------|----------|----------|----------|
| 1st experiment | 1 | 1.7 | 2.7 |
| 2nd " | 1 | 2.3 | 3.0 |
| 3rd " | 1 | 2.3 | 3.0 |
| 4th " | 1 | 3.0 | 3.0 |
| 5th " | 1 | 2.3 | 3.0 |

The growth of sensitiveness is here evident; keeping longer than this appears to give no practical increase. We will try and explain this, but it may be due to some other cause. The editor of the *British Journal of Photography* explains it on the supposition that ammonia is formed in the gelatine by keeping it, and that this re-acts on the bromide. From what we have said before, this will be seen not to be our view; the amount of ammonia formed would be very small, and as the water is in the jelly, the solvent action would not come into play. Again, another point is that we have found that if the emulsion be slightly acidified the same result is obtained, though more slowly, which is decidedly against the ammonia theory. Our own belief is that silver bromide, to be in the most sensitive

state, must be placed entirely beyond any state of strain.* It is during boiling that this strained state is probably given to the particles of silver bromide, and by subsequently keeping the emulsion in a state of jelly this strain wears off, in a similar way to that in which glass is annealed by being kept in a semi-plastic state. When the bromide is in dried gelatine it exists in the same state of strain as that in which it finds itself before the plate is dried. When emulsion which has not been kept is spread on a plate, and one part rapidly dried and the other more slowly, it will be found that the part most rapidly dried is less sensitive than the part more slowly dried. In the one case the strain is taken off, and in the other it is not. In the case of an emulsion kept two or three days, the difference in sensitiveness of the slow and quick drying portions of the plate is not apparent. Another cause of apparent diminution in sensitiveness is the use of too hard a description of gelatine, and also the use of too small a quantity of water with it. The capacity for sensitiveness is present, but it cannot be utilized. The diminution of sensitiveness is here also probably due to the strain on the bromide. We made some interesting experiments regarding this. We had some plates, the emulsion for which was prepared in a very small quantity of water, and the gelatine was very hard. Half of some plates were immersed in water for half an hour, and half of others in a mixture of 1 dr. of glycerine to half a pint of water for the same time. The plates were then dried, and exposed. Those portions of the plate which had been wetted with glycerine and water developed out with proper density; the difference with those wetted with water alone was not so marked; the other portions lacked vigour, and were apparently insensitive. To prove whether the sensitive-

* We would invite a comparison of the effect of light on silver chloride in the crystalline state as produced by fusion, and in the powder state; even when prepared with an excess of chloride, the latter will darken, whereas the former remains nearly unchanged.

ness had altered by the wetting, plates were exposed, then half of them wetted, dried again, and then developed. There was nearly the same result as before. It will be seen, then, that to get a proper amount of density and sensitiveness, the gelatine in the emulsion before coating the plates should have a liberal supply of water with it. Various other experiments have been made, all tending to prove that if great sensitiveness is required, the gelatine should be as soft as is consistent with safety.

Another point which is conducive to sensitiveness should be attended to. If the solution in which the silver bromide is boiled be very viscous, the modification will not take place with any degree of rapidity; on the other hand, fog is induced by having the gelatine too dilute, since the particles are built up too coarsely. With the ammonia process, the above holds good, for if an emulsion be formed in cold solutions, according to Eder's plan, with the minimum amount of gelatine, it will be more sensitive by many degrees than if mixed warm with the full amount of gelatine, and digested afterwards for an hour.

There is one other important factor as to the cause of sensitiveness in a gelatine emulsion plate, and that is the fact that the bromine absorbent, which in this case is gelatine, is in very close contact with the particles, and we might even affirm that it is in close contact with the molecules. For whether the boiling process or the ammonia process be accepted, a certain amount of silver bromide, as we have said before, dissolves, and is reprecipitated whilst in a gelatine solution, and we can scarcely conceive that such should take place without a precipitation of a gelatine molecule or molecules with it. In every particle built up we should then have silver bromide and gelatine in molecular contact, and the bromine absorbent would be in the most favourable position to do its work. In a collodion emulsion, on the other hand, the cotton is not colloidal, and a microscope tells

us that the particles of bromine lie in the interstices of the cotton, and the cotton is not a bromine absorbent. True, when we use a preservative over a collodion film we have a bromine absorbent present, but it is only in contact with the particles, and not with the molecules which make up the particles. When a preservative is rendered strongly alkaline by ammonia, we do have increased sensitiveness, and this is probably due to the bromide being dissolved and re-precipitated, the presence of the bromine absorbent, particularly if it be a colloidal body, such, for instance, as albumen.

CHAPTER VII.

SILVER IODIDE AND CHLORIDE IN EMULSIONS.

THERE has been some dispute regarding the advantage of the use of silver iodide in gelatine emulsions; but we think we may say that its value is at the present time scarcely disputed by any of the advanced workers in emulsion making. The introduction of iodide into rapid gelatine emulsions was first generally brought to the knowledge of the photographic world in a paper read before the Photographic Society of Great Britain, by the writer of this work. At the time, the idea of its being useful was energetically disputed by Dr. Eder and others, and certainly the experiments he brought forward tended to support his conclusion. On the other hand, the experiments made by the writer showed its use.

Two emulsions were made according to Eder's first formula; the second containing about 10 per cent. of potassium iodide, and called I. and II. Two emulsions were made according to Eder's second formula,* one also containing about ten per cent. of potassium iodide, and called III. and IV.

A variety of emulsions were made and tested one

* These methods will be found in a subsequent chapter.

against the other in many ways. We give, in a tabular form, some of the results:—

| | | | | |
|--------------------------------|-----|-----|-----|-----------|
| No. I.—Potassium bromide | ... | ... | ... | 93 grains |
| Swinburne's No. 2 isinglass | ... | ... | ... | 30 " |
| Nelson's No. 1 photo. gelatine | ... | ... | ... | 120 " |
| Water | ... | ... | ... | 2½ ozs. |

And emulsified with—

| | | | | |
|----------------|-----|-----|-----|------------|
| Silver nitrate | ... | ... | ... | 115 grains |
| Water | ... | ... | ... | 2½ ozs. |

| | | | | |
|--------------------------------|-----|-----|-----|-----------|
| No. II.—Potassium bromide | ... | ... | ... | 93 grains |
| Potassium iodide | ... | ... | ... | 10 " |
| Nelson's No. 1 photo. gelatine | ... | ... | ... | 120 " |
| Swinburne's No. 2 isinglass | ... | ... | ... | 30 " |
| Water | ... | ... | ... | 2½ ozs. |

And emulsified with—

| | | | | |
|----------------|-----|-----|-----|------------|
| Silver nitrate | ... | ... | ... | 127 grains |
| Water | ... | ... | ... | 2½ ozs. |

These had been made according to Dr. Eder's formula, with ammonia.

Nos. V, VI, were made with the above formulæ, but boiled with 15 grains of gelatine for half-an-hour; 105 grains of No. 1 photographic gelatine and 30 grains of Swinburne's isinglass were dissolved in 2 ounces of water, and added to them. They were each divided into two parts, and one-half of each was digested with 1 drachm of strong ammonia, as in experiments III and IV. The other halves were washed without having been digested with ammonia. All were allowed to set, and then washed as usual. Those portions of V and VI of the emulsions treated with ammonia we will call Nos. VII and VIII respectively.

Plates were coated with all the emulsions: 1st, on the same day on which the washing was complete; 2nd, on the day after, and then tested one against another. It

may be convenient to call the greatest sensitiveness 10, and to show the others by lower numbers. We find the following results :—

| | | | | | | |
|----------|-----|-----|---------|-----|-----|----|
| No. VI | ... | ... | 2nd day | ... | ... | 10 |
| No. VIII | ... | ... | 2nd day | ... | ... | 10 |
| No. V | ... | ... | 2nd day | ... | ... | 9 |
| No. VII | ... | ... | 2nd day | ... | ... | 9 |
| No. VII | ... | ... | 1st day | ... | ... | 8 |
| No. VIII | ... | ... | 1st day | ... | ... | 7 |
| No. IV | ... | ... | 2nd day | ... | ... | 6 |
| No. III | ... | ... | 2nd day | ... | ... | 6 |
| No. IV | ... | ... | 1st day | ... | ... | 5 |
| No. III | ... | ... | 1st day | ... | ... | 5 |
| No. VI | ... | ... | 1st day | ... | ... | 5 |
| No. V | ... | ... | 1st day | ... | ... | 5 |
| No. I | ... | ... | 2nd day | ... | ... | 4½ |
| No. II | ... | ... | 2nd day | ... | ... | 4 |
| No. I | ... | ... | 1st day | ... | ... | 3½ |
| No. II | ... | ... | 1st day | ... | ... | 3 |

It may be convenient to remember that the odd numbers contain bromide alone, and the even ones *iodide* with the bromide.

It will be seen, when boiling with a small quantity of gelatine (Nos. V, VI, VII, and VIII), that on the second day the plates containing iodide (VI and VIII) have a little advantage over those which contain bromide alone, and that the digestion with ammonia (VIII) gives no increase in sensitiveness.* The same is apparent with VII and V; the digestion with ammonia does not increase the sensitiveness with pure bromide. The first day's plates (VI and VIII) with the iodide are in every way behind the second day's plates with the bromide alone; but evidently digestion with ammonia answers partly the same end as

* It should be said that Mr. W. K. Burton, who is a most careful experimenter, states, in a more recent communication to the Photographic Society, that increased sensitiveness is given.

keeping the emulsion. The same applies also to Nos. I and II. Boiling with a small amount of gelatine, then, in every case, is better than boiling with a full quantity of gelatine, and then digesting with ammonia; but this plan is far better than digesting with ammonia alone. These formulæ are comparative ones, since they all contain eventually the same amount of bromide of silver, and the same amount of gelatine.

As regards development, the plates containing the iodide were a little slower in coming out; but, on the other hand, they were certainly much brighter and cleaner.

To test the value of the iodide further, the same formula as Nos. III and IV were used, and the emulsions brought to the boiling-point when the ammonia was present. No. III fogged; No. IV remained quite bright. The ammonia undoubtedly makes plates much more rapid than when no boiling is attempted; the sensitiveness in which case might, perhaps, be represented as 1 on the same scale as that given before; but it by no means gives the most rapid kind of plate. We think for comparatively slow plates, where good density is required, Formula No. II is excellent in every way; and if any one has a prejudice against iodide, let him use No. I.

It will thus be seen that we hold to introduction of iodide into an emulsion; except for experimental purposes, we never omit it, believing it to be a sheet-anchor for obtaining good and unfogged pictures. We are aware that several commercial makers of plates which have a great name in the market use the iodide, and if those who condemn it would but give it a fair and unprejudiced trial, we should have no fear of making converts of them to its introduction.

CHAPTER VIII.

GELATINE.

IN gelatine emulsions one of the most prominent features is the gelatine, and it is by no means unimportant what kind is selected. Dr. Eder has made long and exhaustive researches on various qualities of gelatine, and Mr. T. F. Elsdén has also thrown light upon its variability in an article in the YEAR-BOOK for 1881, and we cannot do better than quote some of their conclusions. Gelatine is compound of glutin and chondrin. The latter is distinguished from the former by its precipitation from an aqueous solution by acetic acid, and its insolubility in an excess of this reagent. Acetate of lead, alum, and sulphates of iron, aluminium, and copper also precipitate it; but not glutin. Mr. Elsdén also remarks that a convenient test for the presence of much chondrin in gelatine is to add a concentrated solution of chrome alum to a solution of 50 grains of gelatine in 1 ounce of water. If chondrin be present in excess, the gelatine will set while hot. Mr. Elsdén further says:—Remembering that gelatine is a mixture of two substances of different composition and properties, it must be expected to find great variation in the behaviour of commercial samples. Most photographic gelatines, however, consist chiefly of glutin, and their general character is not, therefore, affected to so

great an extent by the small quantity of chondrin usually present in addition.

Gelatine is extremely hygroscopic, and contains, at ordinary temperatures, from fifteen to twenty per cent. of water. In cold water it swells up, and absorbs from five to ten times its weight of water; good gelatine will absorb enough cold water to dissolve it, if the temperature is raised above 90° F. Very weak solutions of gelatine will solidify to a jelly when cold, sometimes when only one per cent. is present; but long boiling destroys, to a great extent, this power of setting.

Gelatine will keep indefinitely in a dry state; but in contact with water it soon putrefies, becoming first acid, and then strongly alkaline, and giving off ammonia; at a temperature of 90° F., decomposition will often begin in twenty-four hours. Hence it is evident that long boiling, besides destroying its power of setting, also tends to produce decomposition of gelatine.

Alum, alcohol, carbolic acid, salicylic acid, glycerine, fuchsin, hydrate of chloral, thymol, and salts of zinc act as antiseptics, preventing the decomposition of gelatine, even in small quantities. If glycerine be used, however, it must be added in rather large quantities. Alcohol and carbolic acid, in large quantities, precipitate gelatine from solution in water.

Acetic acid, hydrochloric acid, sulphuric acid, and oxalic acid dissolve gelatine even in the cold.

Acetic acid dissolves gelatine with great facility, whilst ammonia acts as a weak solvent.

Sugar promotes the solubility of gelatine, whilst gum, in the presence of acetic acid, renders gelatine less soluble, owing to the formation of a compound of gluten with arabic acid.

Silver nitrate, exposed to sunlight in contact with gelatine, causes a red discolouration, due to the combination of organic matter with a sub-oxide of silver.

Chrome alum renders gelatine insoluble; but long boil-

ing and hot dilute acids, potash, potassium permanganate, are able to dissolve the mixture. Alum raises the melting point, but does not render it insoluble.

The quality of gelatine may be tested in several ways. Dr. Eder, among other tests, recommends that the gelatine be incinerated, and the ash weighed, and he says that this varies from $\frac{1}{2}$ per cent. in good samples to 5 per cent. in inferior kinds of gelatine, and to 10 per cent. if adulterated with alum. Our own researches in this matter give a greater margin for good gelatines, 2.5 per cent. being the ash of a certain gelatine which is excellent. We detail some results in the table below. Another test which should be applied is the amount of water it can absorb. Good gelatine should absorb five to ten times its weight of water. A very simple way of testing is to measure out (say) 2 ounces of water, and soak 50 grains of gelatine in it for some hours until it is thoroughly swelled. The water not taken up should then be poured off into a measure, the gelatine being very gently pressed against the side of the vessel in which it was allowed to swell. The amount taken up is, of course, the difference between the 2 ounces, and the amount returned to the measure. A more scientific method is to allow the gelatine to take up as much water as it can at a fixed temperature, drain it, and surface dry it on blotting-paper, and then weigh it. This is a more tedious method than that given above.

| Name of Gelatine | Ash, per cent. | Water absorbed by 50 grains. |
|-----------------------------------|----------------|------------------------------|
| Coignet's gold label gelatine ... | 1 nearly ... | 7 drachms |
| „ special gelatine ... | 1 „ ... | 7 „ |
| Nelson's No. 1 photographic ... | 2 „ ... | 5 $\frac{1}{2}$ „ |
| „ opaque ... | 2 „ ... | 8 „ |
| „ amber ... | 1 „ ... | 4 „ |
| Ordinary French (not branded) | 2 „ ... | 6 „ |
| Swinburne's No. 2 patent ising- | | |
| glass ... | 1 „ ... | 5 $\frac{3}{4}$ „ |
| Cox's gelatine in packets ... | 1 „ ... | 4 $\frac{3}{4}$ „ |

| Name of Gelatine. | Ash, per cent. | Water absorbed by 50 grains. |
|--|----------------|------------------------------|
| Russian isinglass | 1 " | 2½ " |
| Gelatine supplied through Mr. Henderson | 2 " | 8 " |
| Simeon's "Winterthur" gelatine | | |
| Heinrich's gelatine | 1 " | 8 " |
| Batty's gelatine | 2 " | 5 " |

The next test is that of solubility. A gelatine which by itself is soluble at a low temperature is unfitted for gelatine emulsions, particularly if the temperature at which it is prepared is at all high, since then it would not set. Take, as an example of this, Nelson's No. 1 gelatine. In warm weather it will dissolve in the water at the temperature of the room in which it is soaked. Take Coignet's gold label as the other extreme, and it will be found not to melt till the vessel has been plunged into water about 110°. As might be expected, as regards setting, these two gelatines are the most opposite. At a temperature of about 75°, No. 1 will scarcely set at all, whereas Coignet's will set in a short time. A further most practical test is by noting the expansion of films of gelatine which have been spread on plates. The greater the lateral expansion in such films, the greater probability there is of such films "frilling," *i.e.*, wrinkling and leaving the plate. The writer has carried out many tests in regard to this point, and the results show that any gelatine can be tested as to its capability of resisting frilling in a very easy manner. Twelve grains of the following gelatines were swelled in half an ounce of water and melted. Quarter plates were coated with exactly half of the bulk of each solution, and allowed to dry under the same conditions as that in which plates are dried in the drying box. The films were then stripped from off the plates, and different portions cut away and accurately measured whilst dry. The films were then allowed to

swell in water, ammoniacal water, or a solution of mono-carbonates of soda and potash, and again measured. The following are the results :—

| Gelatine. | | Dry. | Water. | Water Carb. Soda and and Ammonia. Water. | |
|------------------------|-----|-------|----------|--|----------|
| | | | | | |
| Nelson's No. 1 | ... | ... 1 | ... 1.2 | ... 1.39 | ... 1.29 |
| Autotype | ... | ... 1 | ... 1.09 | ... 1.28 | ... 1.21 |
| Heinrich's | ... | ... 1 | ... 1.08 | ... 1.22 | ... 1.15 |
| Simeon's | ... | ... 1 | ... 1.05 | ... 1.14 | ... 1.09 |
| Batty's | ... | ... 1 | ... 1.32 | — | — |
| Nelson's X opaque | ... | ... 1 | ... 1.19 | — | — |
| Crosse and Blackwell's | ... | ... 1 | ... 1.09 | — | — |
| Nelson's amber | ... | ... 1 | ... 1.43 | — | — |

An important test is for acidity or alkalinity. For our own part we strongly recommend a gelatine which is *slightly* acid where an emulsion is to be boiled, and if not in this state, we acidify the gelatine solution. When the ammonia process is used, the condition of the gelatine does not matter so much. In some gelatines, the acidity (due to the hydrochloric acid used in its manufacture) can be tasted by applying a piece to the tongue. A hard gelatine can be at once identified when it is set after dissolving in the water, which it will absorb. Any exact determination by applying weight to see where crushing begins is misleading, unless the temperature is uniform during all experiments.

We would here remark that gelatine has an affinity for iodine, bromine, and chlorine, with each of which it combines; hence it is a preservative in the true sense of the word.

The less fatty matter present the better, since it gives rise to opaque spots on development, or else to scum-markings on the plate. Where there is fatty matter present, it may be got rid of by precipitating it in a fine stream in alcohol, or by dissolving it in the quantity of water which has to be used, and skimming it; or by

making it set, and, with a clean ivory knife, cutting off a thin layer from the top.

To select suitable gelatine for an emulsion, we recommend that a small batch of emulsion be made with the specimens proposed to use, and that a few plates not smaller than 7 by 5 be coated and tested before taking it into use for larger quantities.

In our own practice we like to use a mixture of two kinds of gelatine—one hard and one soft, and the proportions of these we vary according to the weather. As a rule, we like 1 part of hard to 2 parts of soft, as it will then set with ease at a moderate temperature, and be hard enough to resist the tendency to frill, and is at the same time readily permeable by the developing solutions.

One fact must also be recollected, that frequent reheating of gelatine speedily detracts from its setting powers, and that if too little water be added to it in mixing, the film has a great tendency to become leathery, more particularly if a little chrome alum has been added to it to prevent frilling. A judicious mixture of alcohol to a gelatine solution increases permeability, and should not be neglected. The use of a sufficient quantity of water is, however, the great desideratum, and should be carefully attended to, the quantity, of course, depending on the temperature at which the plates have to be prepared; thus, in winter, more water should be used than in summer. A very horny, glassy, film is objectionable in many ways, and a moderately matt surface for the plates should be aimed at. This depends almost entirely on the gelatine that is used, and at what temperature it is added, unless it be modified by additions such as glycerine, to which we may at once say we object, on account of its affinity for water.

It will be noticed that ammonia causes much greater expansion than the carbonate of soda (the carbonate of potassium gives almost identically the same results), and the soda more than plain water. It is easy at once to see

which gelatines would be most likely to cause frilling in plates. The absorption of water does not coincide in all cases with the expansion, but this we lay to the different stress put on the different layers of gelatine during the drying.

CHAPTER IX.

GELATINO-BROMO-IODIDE EMULSION.

WE propose to give a detailed account of making an emulsion at ordinary temperatures, say up to 65° Fahr., which may be taken as a pattern on which to form others by any other formula. It will be found to be exquisitely sensitive to the blue rays, and very slightly to the yellow, which latter quality means that the development and preparation of the plates can be conducted in a room fairly illuminated with orange light. To prepare the windows for this, the window may be glazed with stained-red glass, or with one thickness of orange and one of ruby glass. If this be undesirable, two thicknesses of common orange packing paper may be employed. The reader should consult Chapter V., on the Illumination of the Dark-room, for further information on this subject; but the reader must remember that tricks cannot be played with the light of the dark-room, such as are admissible when the comparatively slow wet process is used. Thus he should see that no light of the wrong colour penetrates at any place; he should pay particular attention, for instance, to the chinks under the door, and in the sashes of the window frame. When he has come to the conclusion that no daylight is entering his room, he may think about preparing the emulsion. First of all, he must make a few

preparations. The jar or bottle in which the emulsion has to be mixed must be scrupulously clean. There should be no patches of old emulsion left on it. If a glazed jar be used, it should be seen that the glaze is not cracked in any way, since fog may be expected if it be. For dissolving the gelatine, &c., we like to use glass beakers with a lip, since they are handy for pouring. These also must be scrupulously clean and dry. The scales in which the weighing has to take place should be examined for dirt (chemical or otherwise), and a few circular filter papers on which to weigh the materials should be at hand. Weighing should never be done* without a filter paper of equal size and weight being placed in each pan of the scale. A saucepan of hot water should be ready in which to place the beakers, &c., in which the different materials have to be dissolved, and care should be taken that it is not too full. It need scarcely be said that all weighing can be done in ordinary light. To commence operations, the following may be weighed out separately and placed on clean† paper after weighing, it being supposed that a dozen or a few more whole-plates are required.

| | | | |
|---|-----|-----|----------|
| 1.—Potassium iodide | ... | ... | 5 grains |
| 2.—Potassium bromide | ... | ... | 135 " |
| 3.—Nelson's No. 1 photographic gelatine | ... | ... | 30 " |
| 4.—Silver nitrate | ... | ... | 175 " |
| 5.—Autotype‡ gelatine | ... | ... | 240 " |

Nos. 3 and 5 are rapidly covered with water, shaken or

* Especially on brass scale pans.

† Any contamination by dirt of any description, and particularly that to be found in a photographer's work room, is almost sure to spoil the emulsion, or at all events its sensitiveness, and to cause endless evils. Hence *clean* paper should be used, and the chemicals should not be left on the benches or table in contact with the wood.

‡ In case this cannot be procured, mix 3 parts of Nelson's No. 1 gelatine with 1 part of some hard kind, such as Heinrich's or Simeon's Sw iss.

stirred in it a few seconds, and the water poured off as quickly as possible. This gets rid of any adherent dust on them. Nos. 1 and 2 are then dissolved in 1 drachm and $1\frac{1}{2}$ ounces of water, respectively. To the solution of bromide (No. 2) 1 minim of strong hydrochloric acid is added, together with sufficient of an iodine in alcohol solution to make it a deep sherry colour. No. 3 is swelled for ten minutes in 1 ounce of water, and then dissolved by heat; No. 4 is dissolved in $\frac{1}{2}$ ounce of water, and heated to about 120° Fahr.

In the dark-room, No. 3 is added to No. 4, and shaken up in a bottle till a perfect mixture is secured. Three-quarters of the solution containing No. 2 is then dropped in little by little, and shaken up after each addition; and then the solution of No. 1 is added to the remaining $\frac{1}{4}$ of the solution of No. 2. The mixture is then added as before. The emulsion should appear of a ruby colour when a thin film of the liquid emulsion is examined by a gas light.

This bromide may be placed in a spray apparatus, which is made as follows:—Bend two thin glass tubes in a

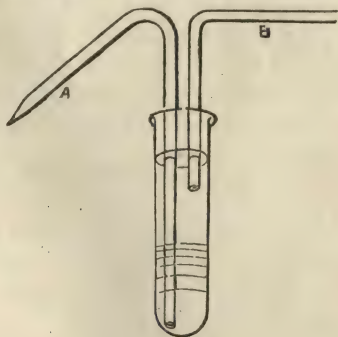


Fig. 13.

common fish-tail burner of the shapes A and B (fig. 13). The tube A should first of all be drawn out so that the

end is perfectly closed; this may be done by the heat of a Bunsen burner, by holding the straight tube over it at about an inch from the end, in one hand, and at any convenient distance in the other, and, when thoroughly softened by the heat at one point, by simply pulling the tube outwards. The glass collapses, and the short bit is pulled off. A flat file is then applied to the point, and the glass filed away till a very small orifice is left. The two tubes are then inserted in a cork, which is fitted into a test-tube as shown. The bromide is placed in the bottom of the tube, and a very fine spray of liquid can be forced through the orifice of A.

The solution of gelatine and silver nitrate should be placed in a glass beaker or a jam-pot, and in the dark-room the spray is blown on to it, and the liquid stirred, at the same time, with a clean glass rod. This gives a very fine emulsion indeed, and, if correctly carried out, a drop of it, when poured on a strip of glass, should show an orange-yellow colour by transmitted daylight, or a deep ruby when a gas or candle flame is examined through it. The possible sensitiveness of an emulsion depends almost entirely on the fineness of grain of the bromide when first formed. With a grey or blue-tinted emulsion extreme rapidity can never be hoped to be attained. The emulsion should be transferred to a 20-ounce bottle,* and well shaken for a couple of minutes, after which it is ready for the next operation.

The method of mixing the silver with the gelatine which we have given above is not practised by most emulsion makers, we believe, though for our own part we have no doubt that it is the best plan of getting the best emulsification with the least trouble. In case the method of mixing the bromide with the gelatine is preferred, the following modification in mixing may be made:—Nos. 1

* Some recommend the use of an earthenware bottle, such as an old ink-bottle. There seems to be no advantage in it, if ordinary precautions be taken for keeping out the light.

and 2 are dissolved in 1 drachm and $1\frac{1}{2}$ ounces of water respectively, and No. 3 is added to the solution of bromide, allowed to swell, and then dissolved. The silver nitrate, No. 4, is dissolved in $1\frac{1}{2}$ ounces of water, and by means of the spray apparatus, or by careful dropping, is added to the bromized gelatine. When half the silver nitrate has been emulsified, the iodide, dissolved in 1 dr. of water, is carefully dropped in, and then the remainder of the silver nitrate is added.

Other Methods of Mixing.—There are other methods of emulsifying which are given here. Mr. England finds that if two 1-drachm measures be filled, one with the bromide solution, and the other with the silver nitrate solution, and then be poured into a bottle together and well shaken, and this operation be repeated again and again till the two solutions are exhausted, he gets a perfect emulsion without grain, and very smooth. It will be noticed that in this plan the silver and the bromide solutions are in equal quantities. Another plan, adopted by Mr. Warnerke (whether it is original with him is not of great consequence) is to draw out two funnels to fine points, and support them on funnel-holders over a jar. These are filled with the two solutions, which are allowed to run into the jar, a stirrer being used to aid emulsification; other workers use the scent-diffuser, by which to secure fineness of grain. Any of these artifices may be employed. A later plan which the writer has adopted, and which is very effective, is to shake the gelatine containing the bromide into a froth, and then to add the silver nitrate little by little. This makes a beautifully fine emulsion, and seems to be equivalent to immersing a delicate film of gelatine into a silver bath, when we know that splendid films are to be obtained, having the very finest grain.

A good *Stirring-rod* may be made by taking a glass rod, and tying across it with clean string a strip of glass about a couple of inches long and half an inch wide. This cross-piece effectually stirs up the emulsion during its

formation by a motion of the rod between the first finger and thumb. We recommend its use.

Boiling the Emulsion.—A saucepan of sufficient size to hold the bottle must be procured, and filled with water to a convenient height, and a flame, such as a gas-burner, placed beneath it.* After the water has been brought to boiling point, the emulsion is kept boiling for 45 minutes; it being shaken at intervals (say once every ten minutes) for half a minute or so. A thick cloth tied round the hand prevents any scalding. The boiling, by-the-bye, should take place without the cork being left in the bottle, for if it remain in, it would be blown out by the force of the steam. A cork with a slot cut in it is, however, not open to objection.

Cooling and Washing the Emulsion.—After the proper time of boiling, the saucepan is removed. The gelatine No. 5 should, as already stated, be rapidly rinsed in several changes of water to get rid of any adherent dust. It should then be placed in a pot with 2 ounces of cold water, and allowed to swell. After this it is melted at a temperature of about 100° , by immersing the pot or flask in hot water, and added to the solution in the bottle. *Both the emulsion, and also the dissolved gelatine,* should be cooled to about 70° to 80° F. by allowing water from the tap to run over the jars before the addition is made.

After a good mixing by shaking, the froth is left to subside, and the emulsion is poured out into a flat porcelain dish,† and allowed to rest. The time which it will take will vary according to the temperature‡ of the surrounding

* To prevent bumping and breaking the bottle, we place half a dozen folds of blotting-paper at the bottom of the saucepan.

† There is no "fetish" in a dish. When the emulsion is to be squeezed, if it is set in a beaker, it turns out in a more convenient shape. In a dish, however, it sets more rapidly, since a greater surface is exposed to the cool air.

‡ In very hot weather, if the dish or jar be stood in iced water, no difficulty in setting will be found. See subsequent chapter for particulars of preparing emulsion at high temperatures.

air, but a couple of hours is generally amply sufficient, and often a much less time will suffice. After a proper consistency is obtained (such consistency being that the gelatine should not tear with a moderate pressure of the finger), the emulsion is carefully scraped off the bottom of the dish with a strip of *clean* glass, and transferred to a piece of very coarse canvas, or mosquito netting, which has been previously boiled in hot water to get rid of any grease or dirt. The character of the canvas and netting can be judged of by the accompanying figures, which are

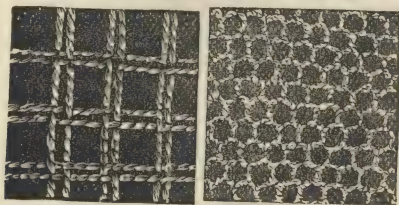


Fig. 14.

of their natural sizes. The emulsion is then twisted up in this, and, by a gentle pressure, squeezed through the interstices, the ball of emulsion being absolutely below the surface of the water into which it is forced. The water causes the threads of gelatine to remain tolerably separate, and, as it passes through the liquid, most of the soluble salts are at once extracted. Some emulsion-makers use a thick ebonite cylinder, over one end of which is stretched silver wire gauze, and into the other is fitted a piston. By placing this piece of apparatus in a screw-press the emulsion is forced through the meshes, and acts like the canvas or netting. For large bulks of emulsion this is certainly the most convenient plan.

When all is squeezed through, the particles of gelatine may again be transferred to canvas, stretched loosely over the mouth of a jar or sieve, and be doused with water from the tap or from a water jug. After a couple of gallons have been thus passed over it, the emulsion should

again be squeezed through the canvas, and the same operation repeated, thus exposing fresh surfaces of gelatine to the action of water. After another sluicing with water the emulsion may be considered as washed, though, to make assurance doubly sure, the gelatine may be left at the bottom of the jar, and the water changed two or three times. We have ourselves found that there is a great gain in using distilled water as the wash water. The gain is not in sensitiveness, but in brightness of the resulting plates. There being no lime in the water, the grease or saponified matter cannot form an oleate of lime, to which we have traced some kinds of spots. To show the importance of thorough washing, the following experiment may be noted. An emulsion was made as above, and after once squeezing through the canvas, a part was immediately used for making plates. A second part of the same was washed under the tap for five minutes; a third part was squeezed and washed a second time; and a fourth part was allowed to soak and squeezed a third time. The relative sensitiveness of the four parts was as follows:

$$1 - 1\frac{1}{2} - 2\frac{1}{2} - 2\frac{1}{2}$$

The first washing increased the sensitiveness to $1\frac{1}{2}$, and the second squeezing to $2\frac{1}{2}$, whilst the third squeezing and washing had no perceptible effect.

The writer considers this method of washing superior to that given below. Two squeezes, it is believed, are equal to twenty-four hours' such washing. Gelatine is hard to permeate, and, being a colloidal body, the crystalline salt has hard work to get through when the emulsion is not finely broken up.

Other Modes of Washing the Emulsion.—There are several modes of extracting the soluble salts from the emulsion. Putting on one side dialysis as introduced by Mr. King, owing to its tediousness, we pass on to the most ordinary method. The emulsion when prepared is poured out into a flat dish in a very thin layer (say) of about $\frac{1}{8}$ of an inch

thick. When set, it is scraped off the dish with a piece of glass, and transferred to a jar or bottle in strips. Mr. England first scores it over with the prongs of a silver fork, so breaking it up into fine strips. Cold water is then poured on to it, and a stream of running water kept flowing over it for twelve hours, more or less.

The writer has converted a tin canister into an effective washing apparatus, as shown in the figure. In the lid of

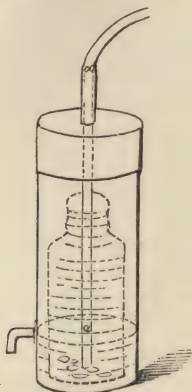


Fig. 15.

a common canister a hole is perforated so as just to admit of the insertion of a glass tube *a, a*; a piece of india-rubber tubing connects this with the water tap, and covers any small chink between the glass and the lid, as shown. A spout is soldered on to the canister, as shown. A bottle containing the emulsion to be washed is placed in the canister, the tube being inserted in it. The water flows over the top of the bottle, and rises in the canister to the level of the spout, where it trickles over into the sink; the heavy water containing the soluble nitrate is thus perpetually stirred up and caused to flow over the neck of the bottle. This answers admirably, and can be used in the daylight if necessary, but is more applicable

to emulsion that has been cut into strips than to that which has been squeezed twice, as the small particles are apt to be carried over the top of the bottle and choke the exit tube. A combination of this method with that given on page 143 can, however, be made by only once squeezing the emulsion through the napless canvas.

Dr. Eder, to whose careful researches photographers are much indebted, finds by absolute analysis that emulsions passed through fine canvas are sufficiently washed in about thirty-five minutes in running water, and nearly in the same time in standing water; through coarse meshed canvas in one and a-quarter hours in running water, and in a much longer time in standing water. When cut in strips, it is probable that twelve to twenty-four hours may be necessary to free it sufficiently from the soluble salts, in order to obtain a maximum sensitiveness.

Precipitation of the Emulsion by Spirits of Wine.—Another method is also due to Messrs. Wratten and Wainwright, and is as follows:—After the emulsion has been allowed to rest for two or three hours, two ounces of alcohol to each ounce of water used are poured into the bottle containing it, and well shaken up. The gelatine rapidly assumes a pasty appearance, and subsides to the bottom. The bottle is then inverted, and the fluid, which contains the soluble nitrates and excess of water, is poured off, and may be preserved for distillation. The explanation of the efficacy of this method is, that the alcohol has a greater affinity for water than has the gelatine, and that in extracting the water the soluble salts are extracted with it. Methylated spirit not containing gum may be used, and the lower the specific gravity the more effectual it is.

Draining the Emulsion.—When the emulsion is considered to be properly washed, it has to be drained. This the writer generally does over the canvas or net used for the squeezing operations, though some recommend a hair seive, but it does not appear that there is much advantage

to be derived from its use. The great point in either case is to drain long enough. A couple of hours is sufficient time, and then the emulsion is ready for melting.

It will sometimes happen that no amount of draining over a hair seive or canvas will render the emulsion sufficiently free from water to set well when dissolved up. We have found that by pouring a couple of ounces of alcohol through the emulsion when draining, that the excess of water is taken up, and it becomes firm. It should be noted that before re-dissolving the gelatine it should be firm and free from all sloppiness (if such an expression may be used); one dose of alcohol generally effects this, and, if not one, two will. The alcohol may be saved if required. In case this artifice be resorted to, only half the quantity of alcohol given before should be added to the emulsion, when it is re-dissolved for filtering and coating the plates. Emulsion that is cut up into shreds is much more easily drained than that which is squeezed through canvas. It is not that the gelatine takes up more water, but that the water clings mechanically to the small particles forming it.

Dissolving the Emulsion.—After draining, the emulsion should be transferred to a clean jar or jam-pot, and then placed in boiling water till all the gelatine is thoroughly dissolved. A temperature of 120° or more may be given it with advantage. The emulsion, when all additions are made, will be about 10 ounces. The addition of $\frac{1}{2}$ grain of chrome alum is to be recommended. This should be dissolved in 1 drachm of water, and added with stirring; 6 drachms of absolute alcohol are next to be added in the same way, and the emulsion is then ready for filtering. This operation may be carried out in various ways. The writer now uses wet chamois leather, or two thicknesses of swansdown calico which has previously been well boiled and washed. This is allowed to rest loosely in a funnel, and the emulsion filters slowly through it, all coarse particles being left behind. It is preferable to filter into

a Florence flask, as it will bear heat, though an ordinary medicine bottle will answer if the flask be not at hand. The bottle or flask is again placed in water at a temperature of 120° , and the next operation is to coat the plates. There is one very remarkable feature about emulsions, which is, the great variation in their covering powers. If a plate be coated and found to give great opacity when the ordinary amount of emulsion is poured on and set, no harm will be done by adding another 60 or even 120 grains of gelatine (which have been swollen in a couple of ounces of water and melted) to it. This of course increases the bulk of the emulsion, and at the same time is economical. As a rule, it will be found that the emulsions which remain of an orange tint by transmitted light after boiling are those which possess most covering power. The reason of this is not far to seek, as the orange emulsion is in finer particles than the blue or violet. This addition should of course be made before filtering.

CHAPTER X.

BENNETT'S GELATINO-BROMIDE PROCESS.

THE next process we shall describe is that brought out by Mr. C. Bennett, and was the first process published (1878) which gives extreme rapidity. His description of it is extracted from the *British Journal of Photography*. Sensitiveness is attained by slow digestion at a low temperature instead of by boiling. Mr. Bennett, after describing the light required for the preparation of the plates, on which we have already written (Chapter IV.), says:—

“To make ‘assurance doubly sure,’ use a ruby-coloured hock bottle, and with two eight-ounce decanter-shaped bottles made of test-tube glass to stand heat, weigh out for a ten ounce solution—

| | | |
|-------------------------|-----|-----------|
| Ammonium bromide ... | ... | 70 grains |
| Best silver nitrate ... | ... | 110 ” |
| *Gelatine ... | ... | 200 ” |
| Distilled water... | ... | 6 ounces |

Use Nelson's ‘No. 1 photographic gelatine,’ for with the opaque sixpenny packets you have irregularity, red fog,

* It will be noted that the gelatine and the silver nitrate have the proportion of twenty to eleven, or nearly two to one. In the bromo-iodide emulsion of Chapter IX. the proportion is four to three, supposing the gelatine in which the emulsion is boiled is destroyed. In developing, it is evident the former will require less restraining than the latter.

and frilling. Place aside four ounces of water for the bromide, and two ounces for the silver; dissolve the bromide with heat in one of the flasks in 1 or $1\frac{1}{2}$ ounces of water; pour into the hock bottle; swill out the test-tube with the remainder of the four ounces set aside for the bromide, and also pour in. I do it by heat to ensure all being dissolved, as it does so very slowly after the gelatine is inserted. The four ounces of solution being now almost cold, add the gelatine, shake up well, and place in two or three gallons of water at 90° . I use a fish-kettle with lid. [A good-sized saucepan with a lid answered perfectly with the writer.] In two hours the bromized gelatine will, after well shaking, be quite liquid, and also nearly at 90° . Now dissolve the silver in the other flask in one ounce of water, cool to 90° , and pour in; use the remainder of the two ounces set aside for the silver to rinse out the flask, heat to 90° , and pour in. By being so particular we get regularity, and are able to mix different batches of emulsion, which is a great boon. Shake the emulsion very briskly, and replace in the kettle for two, four, or seven days, according to rapidity required. The temperature should never be over 90° ; if you do not let it exceed that, you will not have red fog. 'Cosy' it up with flannel, and it will not lower many degrees during the night. I, however, use a stove two feet across, and place it on that; a faint gas jet below keeps it always at 90° . I shake up every twelve hours. If washed in two days, the emulsion is rapid and dense; in four days, more rapid and less dense—quick enough for any drop-shutter known, when developed as below. With some that I kept for seven days, with drop-shutter, on a dull February morning, pebbles close to the camera were perfectly exposed. The negative was thin under ammonia, but bore intensifying to any extent.

"Cool the emulsion in a bottle not smaller than a Winchester quart, and wrap it up in brown paper to exclude all light except the lip of the neck. Let an india-rubber

tube go quite to the bottom of the bottle to stir away those layers of water which, on account of greater specific gravity (by reason of the salts they now contain), would otherwise remain there. Wash for twelve hours; a dribble is sufficient. Upon melting you have eight or nine ounces of emulsion; add three-quarters of an ounce of pure alcohol heated to 90° ; fill up with water (also warm) to ten ounces, and coat. The plates should be only lukewarm, or you will have red fog. For beginners it much helps the coating to double the quantity of alcohol, leaving out water to that extent. The operator should not be alarmed at the peculiar mottling of the film (due to the alcohol) directly after coating; this subsides in a few seconds to an even surface. The extra alcohol does not appear to alter the sensitiveness, and is a great help; but with experienced workers it is not necessary, and the quantity is sufficient to draw the emulsion up to the edges, which is the sole object of introducing it. When no alcohol is used you always have *thin* edges, which is very objectionable, as the negative, of course, will print dark at those parts, and this small addition of alcohol totally rectifies this fault. It is difficult to measure the exact quantity of emulsion required for each plate; one ounce would probably cover *eight* plates of $6\frac{1}{2}$ by $4\frac{3}{4}$ size."

CHAPTER XI.

PAGET PRIZE EMULSION.

THE following is the description of the process sent in by Mr. Wilson, which won the Paget Prize Competition in 1880 :—

To make a pint of emulsion—

Select a 20-ounce narrow-mouth stoppered bottle, with a well-fitting stopper, and thin bottom. Make it perfectly clean.

Make a stock solution of—

| | | |
|--------------------------|-----|----------------|
| Hydrochloric acid (pure) | ... | 1 fluid drachm |
| Distilled water | ... | 12½ ounces |

Put into the 20-ounce bottle—

20 minims of the above *dilute* acid.

3 fluid ounces distilled water.

210 grains ammonium bromide.

80 grains Nelson's No. 1 Photo. gelatine.

Leave the gelatine to swell for (say) fifteen minutes or longer.

The Addition of a Trace of Hydrochloric Acid to the soluble bromide and gelatine is recommended in the formula given, for the following reasons :—If the soluble bromide be absolutely neutral, and the gelatine a suitable sample (see

page 65), the hydrochloric acid is *not necessary*, and better omitted. If, however, the gelatine be ever so little alkaline, or even apparently neutral, but yet does not give a clear solution, acid is required. Its use is not to produce silver chloride, but to ensure a fine precipitate of silver bromide. According to Mr. Wilson's experience, a fine precipitate is hardly at all a question of the method of mixing, and elaborate contrivances for the purpose he considers as quite unnecessary. A fine precipitate is easily obtained, however rapidly the solutions be mixed, if two conditions exist, viz., if the bromized gelatine solution contain a trace of hydrochloric acid, and the *silver* solution be not stronger than 110 grains per ounce. If it be 50 to 60 grains per ounce, it may be poured in all at once; or if a little weak solution be first poured in, the stronger may follow (as per formula). A good test for the suitability of a gelatine is to see if a fine precipitate can be obtained without having to add hydrochloric acid. Too much hydrochloric acid retards or prevents the conversion of the silver bromide into the sensitive form in cooking; a large excess destroys the gelatine.

It will thus be seen that the addition of hydrochloric acid must be made *intelligently*, according to the other materials accessible.

It might be supposed that any acid would make the precipitate fine, and that, therefore, acid ammonium bromide would be good. Such is not the case, and, moreover, the acid bromide has in some way a powerful effect in retarding the conversion of the silver bromide into the sensitive form.

Ammonium Bromide should be as nearly as possible *neutral*. It is usually more or less acid, even though otherwise pure, and frequently becomes strongly acid by keeping. It is then quite unfit for use, and will not give good results unless almost neutral.

Since sending in the formula for competition, Mr.

Wilson has arrived at the conclusion that, on the whole, it is better to use bromide of potassium. The latter is often alkaline, but may, without much difficulty, be obtained neutral, and is free from tendency to alter.

Silver Nitrate is usually—if good—slightly acid with excess of nitric acid. It may be so used; but it was recently found that better results are obtained if the silver solution be neutralized with carbonate of soda. A slight excess does no harm, as the resulting trace of carbonate of silver is converted into bromide; indeed, emulsion *may* be made by mixing washed carbonate of silver with a soluble bromide.

The uses of neutralizing the silver are twofold. One is, that as the amount of acidity of silver nitrate varies with different samples, it ensures the same conditions in all cases; the other is, that the presence of nitric acid in an emulsion produces a tendency to green and pink discolourations in the finished negative.

In a clean glass vessel (beaker, measure, or flask) dissolve 330 grains nitrate of silver (re-crystallized) in 3 ozs. distilled water.

Pour out about 2 fluid drachms of this silver solution into another small vessel (say test tube), and dilute it to half strength with an equal quantity of distilled water.

Take the 20-ounce bottle and the two lots of silver solution into the dark room. Mr. Wilson prefers to use a large paraffin lamp, protected by one thickness of ruby and one of dark orange glass, to two thicknesses of dark orange paper without any ruby.

In the dark room have a gas-boiling stove, and on it a tin pot or saucepan deep enough to contain the bottle when the lid is on. It should have a tin perforated false bottom, to prevent the bottle resting immediately on the true bottom; or a piece of wire gauze will answer. Let the pot contain some three or four inches in depth of *boiling* water.

Turn out the gas of the stove, if alight, and plunge the

bottle into the water two or three times, so as to avoid cracking it by too sudden heating; then leave it in for a few minutes until gelatine is completely dissolved. Do *not* leave it in longer than necessary for complete solution. Take it out, shake up, remove the stopper, and set bottle down on table near your lamp, so that you can see what you are doing.

Pour in *all at once* the four drachms of *dilute* silver solution. Put in the stopper and shake up thoroughly, but not too violently, for about half-a-minute. Now pour in the strong silver solution in quantities of about half-an-ounce at a time, shaking as before after each addition, and, when all is added, give a final thorough shaking for (say) a couple of minutes.

If the instructions have been so far accurately followed, there will be no coarse precipitate or grit in the finished emulsion.

Now put the bottle into the pot of hot water, see that the stopper is not jammed in, and put on the lid. Light the gas, and boil up as quickly as possible. If the water was previously boiling, and the gas only turned out for the mixing operation, it should boil up in less than five minutes; then keep boiling for *fifty-five minutes*. At the end of this time turn out the gas, take off the lid, take out the bottle, and remove the stopper *at once*, or you will not get it out afterwards. The bottle must now be cooled down as quickly as is consistent with safety to the glass. In very cold weather it may stand on the table for ten minutes or so, and then be cooled with water; or in any weather, place it in a pan of nearly boiling water, and cool gradually by allowing cold water to trickle slowly in, shaking the bottle occasionally. Whatever method is adopted, it should be down to 90° F., or lower, in fifteen or twenty minutes at most. It cannot easily be made *too* cold, as the gelatine has lost its power of setting.

In a glass beaker (about 12 or 14-ounce size) put

1 ounce of Nelson's No. 1 Photographic or "X opaque" gelatine, and pour over it 10 ounces of clean ordinary water. Leave it to soak until the gelatine has absorbed 4 ounces of water, pour off the surplus 6 ounces, melt the swelled gelatine by immersing the beaker in hot water, and pour it into the 20-ounce bottle containing the cooled emulsion. Shake up well, and pour all back into the beaker, draining out the bottle thoroughly. Leave it to set in a cool place. Mr. Wilson prefers to leave it for twenty-four hours. It has next to be washed.

The Addition of the Gelatine after boiling should be made when the boiled emulsion and dissolved gelatine are both at as low temperature as possible, and between the time of this addition and that of washing the emulsion, it should be kept as cold as possible. The reason of this appears to be that the excess of alkaline bromide has a most destructive effect on the new gelatine, and therefore the lower the temperature and shorter the time during which the two are in contact, the better.

There is a curious effect depending on the temperature at which the emulsion and fresh gelatine are mixed, viz., that if quite cold the resulting plate will have a matt surface, and the higher the temperature the more glossy it will be.

A plain solution of gelatine in pure water is very little injured by prolonged boiling; but if an alkaline bromide (or chloride) be added, it is speedily decomposed. Probably the alkaline nitrate, which is present in the emulsion in large quantity, may be even more effective.

For the washing, clean ordinary water at a temperature not over 50° F. should be used. The writer prefers at all times to use water cooled down to below 40° by melting ice in it. By so doing, uniform results are obtained, and where ice can be procured the cost is trifling; 3 lbs. of ice will be sufficient for a pint of emulsion in the hottest weather.

In a glazed earthenware pan or other suitable vessel,

put about 3 pints of cold water, and add 3 ounces of saturated solution of potassium bichromate (made by saturating clean ordinary water with the bichromate.

Before squeezing the set emulsion through the canvas, it should be cooled down so as to be as firm as possible. The water into which it is squeezed will then remain almost clear, or but slightly milky. If the *emulsion be soft*, even though the *water* be ice cold, the water will be more milky, and the emulsion take up too much. Too much excess of acid bromide, too high a temperature at the time of adding the gelatine, or keeping at too high a temperature between adding and washing, will produce the same result.

The emulsion may, of course, be washed by precipitating with alcohol, squeezing the clot, breaking it up, and soaking in water; but the writer prefers washing with water and bichromate, as described, on account of the clear and brilliant shadows so obtained.

Having cooled the beaker of set emulsion down to 40° F., run a bone spatula or paper knife round, and turn out the emulsion, or cut it out in lumps. If cold, it will come out almost quite clean from the glass. Place it on a piece of coarse "straining cloth" or canvas, and squeeze through the meshes into the water, the operation being performed under the surface of the water. Leave it so for an hour. Lay the straining cloth over the mouth of another pan or large jar, and pour the mixture of emulsion threads and liquid on to it so as to let the latter run through. Squeeze the emulsion a second time through the cloth into clean cold water, and immediately repeat the operation a third time, leaving the emulsion in the last water for half an hour. When strained for the last time, place cloth and all in a large beaker, and put the latter into hot water until the emulsion is completely melted and warmed to about 115° F., *i.e.*, not warmer than is pleasant to the hand. With a *clean* hand take out the cloth and squeeze it; very little will be lost. The emulsion should now

measure about 16 or 17 ounces. Add 2 ounces alcohol, and mix thoroughly. The alcohol may be either pure ethylic alcohol, sp. gr. about .830, or *good colourless* methylated spirit. The writer prefers the former. If the emulsion now measures less than 20 ounces, make it up to that by adding clean water.

A good deal depends on the temperature at which this is done, and by careful management much may be effected. If the emulsion is sufficiently rapid, and free from green fog, it is best melted and coated at a low temperature. If it be slow and has a tendency to colour, it will be improved by heating to 140° F. Mr. Wilson has had emulsions which became more than three times as rapid by this treatment; but it is a somewhat dangerous one, as too high a temperature, or too prolonged heating, may result in hopeless grey fog. This kind of fog is more apparent during development than after fixing.

The emulsion is now ready for use. It should be filtered into the coating-cup through cotton-wool to free from bubbles, and plates coated in the usual way, dried and used as usual for rapid gelatine plates, using about an ounce of emulsion for a dozen quarter-plates.

In drying arrangements, avoid the contact of gas, or of the products of combustion of gas, with the moist plates. The writer finds both to be very injurious.

The exposure is the same as for fairly rapid gelatine plates, and the development may be conducted by any of the methods to be described in a subsequent chapter.

CHAPTER XII.

BURTON'S PROCESS.

MR. BURTON more recently worked out a process which certainly simplifies the washing of an emulsion, but which at the same time is rather more expensive, in that it requires the use of spirits of wine or methylated spirits for precipitation purposes. Mr. Burton kindly forwarded a statement of his process, and we give it as he has described it. He prepares the following solutions:—

| | | | |
|---|-----|-----|------------|
| 1.—Silver nitrate | ... | ... | 212 grains |
| Water | ... | ... | 1½ ounces |
| 2.—Ammonium bromide | ... | ... | 120 grains |
| Ammonium iodide | ... | ... | 10 „ |
| Gelatine (Nelson's No. 2 photo- graphic) | ... | ... | 30 „ |
| Hydrobromic acid | ... | ... | 1 drop |
| Water | ... | ... | 1½ ounces |

These are emulsified as given in Chapter IX., at page 72, or by shaking in a bottle as described at page 73. There is no reason why the precipitation should not take place by the reversed method (page 71), and we recommend it.

The emulsion is boiled as given at page 74, and is then allowed to cool to about 50° or 60° F. It is then poured in a stream into 6 to 10 ounces of alcohol, the quantity depending on the specific gravity of the spirit used; 6 ounces of absolute alcohol suffice, whilst it is safe to use

10 ounces with ordinary methylated spirit, since it usually contains a large quantity of water. The emulsion settles down to the bottom of the vessel in a few seconds in the shape of a dense flocculent precipitate. Most of the soluble salts are, of course, at once extracted, but it is better to wash it further, either by decantation, or by placing it on a hair-sieve in running water; the precipitate is coarse enough not to pass through the meshes.

In the meanwhile the following has been prepared and made into a solution:—

| | | | |
|---------------------------------|-----|-----|------------|
| Nelson's No. 2 gelatine | ... | ... | 120 grains |
| Autotype or Swiss hard gelatine | ... | 150 | " |
| Water | ... | ... | 12 ounces |

The bromide of silver precipitate is added to this, and well shaken till it is dissolved and all granularity has disappeared.

The difference between this mode of washing and that originally described by Wratten and Wainwright (see page 78) is, that in the one case the emulsion containing all the gelatine is precipitated, and in the other but a small quantity of gelatine has to be thrown down, and consequently the elimination of the soluble salts in the latter case is far more perfect. There is also a saving in alcohol. To prepare an emulsion in the shortest possible time, this process meets the requirement, since it saves much time in washing, and all the time of draining.

Again, too, it will be seen that this is a capital plan of preparing dry pellicle which will keep indefinitely, and the bromide will remain in its most sensitive condition, since, after precipitation and washing, it will rapidly dry, as the bulk of gelatine is so small, and is in a granular state.

Mr. Burton recommends the use of acid, as it gives what he happily calls a "robust character" to the emulsion; that is, that the plate will stand more rough usage, and more forcing in development.

CHAPTER XIII.

DR. EDER'S PLANS OF PREPARING GELATINE EMULSIONS WITH AMMONIA.

ONE of these methods is based on the utility of allowing ammonia to re-act upon the bromide of silver in its original condition, which enables the sensitive emulsion to be formed more rapidly than by Monckhoven's method. The second method, by which greater sensitiveness is obtained, consists in boiling the gelatine emulsion by itself, and subsequently treating with ammonia at 95° F. for half an hour. We quote Dr. Eder's own words (see *Photographic Journal*, November 19, 1880).

I. *Method with Ammonio-Nitrate of Silver.*—This method furnishes very sensitive plates, which are at least six or seven times as sensitive as wet plates. The necessary operations are simple and quickly executed, requiring but few apparatus and arrangements, and may be effected without continued warm digestion. The requisites are an ordinary cooking-pot, a spirit lamp, a thermometer, and a reliable dark-room. The plates show great power and density, and keep wonderfully clear. The emulsion works so clean, and is so free from granulation, that not only landscapes and portraits can be taken with it, but reproductions of line drawings can

be made without intensification. The following is the formula he recommends:—

| | | |
|--------------------------|--------|--------------|
| No. 1.—Potassium bromide | ... | 370 grains |
| Gelatine | | 520 to 700 „ |
| Water | | 10½ ounces |

This is dissolved (as given at page 139), and raised to a temperature of from 95° to 120° F.

| | | |
|-----------------------|--------|------------|
| No. 2.—Silver nitrate | | 460 grains |
| Water | | 10½ ounces |

Into this latter is dropped strong liquor ammonia till the precipitate is just re-dissolved, and it is then, in a ruby light, added drop by drop to No. 2, and shaken. The flask containing the latter solution is rinsed out with 1½ ounces of water, and the emulsion is then placed in a water-bath at a temperature of 95°, for from a quarter to half-an-hour, gradually allowing it to cool down to 75°, but not lower.

The salts and the gelatine do not require to be so carefully chosen for this method as for that which follows. Should the bromide of potassium have an alkaline reaction it does no harm in this method; neither is the neutrality of the nitrate of silver imperative, nor the acidity of the gelatine; indeed, it may be alkaline.

The specific gravity of the ammonia, regarded as a determinant of its strength, is a secondary consideration. Take a strong solution of ammonia. The proper quantity is defined sharply enough by the words—“as much ammonia as will re-dissolve the precipitate produced in the nitrate of silver solution.” As one is deprived of this indication by which to regulate properly the addition of ammonia, whenever one adds the ammonia to the gelatine containing bromide of potassium (instead of to the nitrate of silver), Dr. Eder does not so much recommend this manner of mixing, though, by the alteration in the procedure, the same sensitiveness is obtained as by

the former method.* Great care should be taken, when adding the ammoniacal silver solution, that the temperature does not rise too high, and that, during the digestion, the water-bath does not become too hot, otherwise fog is sure to result. The temperature should never exceed 105° F.

When the digestion is finished, the emulsion should be poured into a glass beaker (one made of not too thin glass) or into a porcelain dish, which is placed in cold water to accelerate the setting. When set it is pressed through canvas as used for Berlin-wool work, and the operation may be conducted as given at page 77, and then washed in frequently-changed (or, better still, running) water for twenty-four or forty-eight hours, whilst suspended in a coarse stuff bag. A great deal of water adheres to the gelatine particles, which should be allowed to drain for at least half-an-hour, either from the bag or else through a cloth filter placed loosely in a large funnel. If this draining be omitted, the emulsion will most likely be too fluid. The superfluous water may also be removed with advantage by gentle pressure.

The finely-divided emulsion may be deprived of water by placing it in a bath of alcohol, and then dried in thin films in the air, either perfectly or only superficially,† or it may immediately be liquefied by heating in the water-bath. Filtration through flannel placed in a warm funnel is good; but it is generally sufficient to allow the liquefied emulsion to deposit any sediment by standing quietly at rest. If it be intended to keep the dissolved gelatine emulsion for some time, an antiseptic must be added. To 10 ounces

* When gelatine, bromide of potassium, and ammonia are dissolved, and the nitrate of silver is then added, the ammonia should not be allowed to act too long upon the gelatine. The ammonia is best added immediately before the addition of the nitrate of silver to the gelatine.

† Dr. Eder stated that he had not tested this method so minutely as to be able to maintain that it furnishes exactly the same product as an emulsion immediately re-dissolved; but that he finds this preparation keeps better than the dissolved aqueous emulsion.

of emulsion add 10 grains of salicylic acid dissolved in 1 drachm of alcohol, or replace the salicylic acid by the same weight of thymol oil, as a protection of the gelatine against change caused by a long warming, putrefaction, &c. Alcohol has a favourable action, accelerating the setting of the gelatine and the drying of the film.

The proportion of bromide of potassium to nitrate of silver is 4 : 5 ; it is not advisable to take less bromide, as there is then a risk of fog. The difficulty of fixing the proportion of the soluble bromide to the nitrate of silver consists in finding the proper medium between the too much bromide, which retards the sensitiveness, and the too little, which it is not possible to overlook, on account of the decomposition of the bromide of silver which sets in, both in the case of treatment with ammonia, and boiling. The proportions mentioned are those which have been found best both by Captain Toth and Dr. Eder.

The conversion of the insensitive modification (which transmits red light) into the extremely-sensitive modification (transmitting blue light) takes place in a very short time when the above directions are followed. Even at a temperature of 25° C. (77° F.), the complete conversion generally takes place in from fifteen to twenty minutes. A small sample poured as a thin film on a sheet of glass is sufficient to test whether the rays transmitted, be they of daylight or of naked gas or candle-light, are blue or not. In the former case the digestion may be stopped. Generally, the prolongation of the digestion over thirty minutes develops no further increase in sensitiveness worth mentioning ; but if the temperature be not raised above the point before mentioned there is, even after three hours' digestion, no danger of fog.

If the liquid be too hot, or the solution too thin (that is to say, too poor in gelatine), or if the added ammonio-nitrate of silver be dissolved in too little water, the bromide of silver will be too coarse in the grain. It then quickly settles at the bottom, and the emulsion becomes

unequally mixed. The negatives also would be coarse-grained, but there would be, nevertheless, no particular increase observable in the sensitiveness.

By the gentle heat prescribed above, the gelatine should not be injured or so changed that its setting power, &c., suffers. It is, therefore, intentionally recommended to add all the gelatine at once. By all methods of emulsification with ammonia the separate addition of most of the gelatine after the washing is completed is impracticable, since the greater part of the gelatine must be added before the setting and washing, in order to impart the necessary solidity to the mass, and a renewed heating of the emulsion in order to dissolve the additional gelatine would be unavoidable. The repeated or too prolonged heating of gelatine emulsion containing ammonia, as is known, is hurtful.

The emulsion must be washed with great care. It is quite impossible to attain the full sensitiveness of the plates in the presence of any considerable quantities of soluble bromide; besides which, the slight residue of ammonia is an enemy to the keeping qualities of dissolved emulsion, because, even in small quantities, it has a corrosive action, and combines with the salicylic acid, subsequently added as an antiseptic, to the great injury of its property of retarding putrefaction.

II. *Method by Boiling and Subsequent Digestion with Ammonia.*—This is more complicated than Method I., and requires more care. It is based on the observation that the modification of bromide of silver which transmits blue light is produced very rapidly at a temperature of from 60° to 100° C. (140° to 212° F.), and that the sensitiveness of such an emulsion—already of itself highly sensitive—can be increased by subsequent treatment with ammonia at a gentle heat, while continued boiling would bring fog.

The proportions of the separate ingredients are the same as in Method I. (see page 94). The emulsion is

then boiled; but during the boiling the cork should not usually be driven in quite tight, for fear of the bottle bursting by the expansion of the steam. When using a common glass bottle, change the ordinary cork for one which has a groove cut in it. The bottle, filled with emulsion, is put in a perfectly light-tight tin saucepan furnished with a tight-fitting lid,* and under the saucepan is placed a gas jet or a spirit lamp, care being taken that not even the reflected light from the spirit flame should fall upon the emulsion. Of course it is understood that the whole operation takes place in the dark room. The boiling is continued for half an hour from the time the emulsion reaches nearly boiling point.

The emulsion already possesses a high degree of sensitiveness (similar to that of the best commercial gelatine plates), and may be used without any further treatment with ammonia. The latter, however, increases the sensitiveness. When the emulsion has become quite cool (the temperature may fall to 70° F.), add to it two drachms of ammonia, s.g. .880, place it in a water-bath of from 95° to 100° F., and digest at this temperature for half-an-hour to an hour. At the end of that time the emulsion is ready, and one then proceeds, after it has set, to wash it, &c.

During the subsequent treatment with ammonia, care must be taken that the temperature never exceeds 105° F. Generally, digestion for half-an-hour suffices, but with an hour there is more certainty of attaining the desired sensitiveness. Even digestion for two hours does not develop fog. The prolongation of the digestion with ammonia is particularly useful when the previous boiling is interrupted before the bromide of silver is sufficiently modified. It is assumed, however, that during the whole process of digestion the water *never sinks below*

* A linen rag laid at the bottom of the saucepan prevents the bottle from cracking in consequence of coming in sudden contact with the hot metal forming the bottom of the pot.

100° F. All the precautions described as applicable to the adding of ammonia (Method I.) also apply here.

Here also all the gelatine must be added at once; it does not do (as in Method I.) to retain a portion, and to add it later.*

With regard to other details (washing, quantity of gelatine, &c.), the remarks made with reference to the last method apply here.

Dr. Eder says that a gelatine emulsion prepared by Method II. is more sensitive than one prepared by Method I. The difference is, perhaps, not extremely great, still the sensitiveness of that prepared by the Method II. ought at least to be a fifth greater than by Method I. It gives negatives with good gradation, and free from that hardness which is often seen in less sensitive emulsions, which are difficult of reduction by the developer. The whole picture generally comes out pretty quickly under the developer, and even when the exposures are very short, the shadows are sufficiently developed before the lighter parts have become too intense. Dr. Eder believes this emulsion will be found particularly suitable for portraiture in the studio. It can be worked to opacity, but is less apt to produce perfectly white and black negatives than emulsion prepared by the first method.

To sum up in a few words:—Emulsions prepared by Method I. are most suited for the production of hard negatives, and those prepared by Method II. for soft negatives. The former has the same character as the most sensitive emulsions at present in the market; the character of the latter is unusual. *Still it cannot be said that with either, both hard and soft negatives cannot be got according to the way they are developed.*

* Dr. Eder, however, expressly mentions that, with very easily-affected sorts of gelatine, part of the gelatine may be beneficially added, when the digestion is completely ended.

In the preparation of emulsions by Method II. great care must be exercised. The gelatine and bromide of potassium should not have an alkaline reaction, for fear of the formation of fog during the boiling. The materials must, therefore, be previously tested with litmus paper.* If the nitrate of silver be added to the gelatino-bromide of potassium, when heated to 60° or 70° C. (140° to 160° F.), the formation of the extremely-sensitive modification is sooner produced.

The ferrous oxalate developer is especially suited to these fairly sensitive gelatine emulsions, though the alkaline developer may also be used; the former gives particularly clear and brilliant negatives.

* Should one not be able to obtain any neutral or slightly acid preparations, the hot solution of bromide of potassium and gelatine may be carefully acidified with dilute acetic acid or hydrochloric. The reaction should be only *slightly acid*, otherwise the acetic acid will destroy the setting power of the gelatine.

CHAPTER XIV.

COLD EMULSIFICATION PROCESSES:

MR. A. COWAN has made a modification of Dr. Eder's process which is certainly the easiest form of the ammonia process, and gives excellent results as regards rapidity.

The same proportions of gelatine, bromide, iodide, and silver are taken as given at page 70, and dissolved up in same amount of water; *the iodine and hydrochloric acid are omitted*, however. The silver should be dissolved in cold water, and the gelatine solution, after dissolving, should be cooled. This can readily be effected by making the vessels containing the different solutions to stand in cold water. To the silver is added sufficient ammonia—equal parts of ammonia (.880) and water—just to dissolve the oxide first formed by the alkali. The bromide and gelatine are then gradually added to the ammoniacal silver nitrate, and a fine emulsion is formed. The remaining gelatine is dissolved in the same amount of water as given at page 74, and its solution also should be cooled down. This is added to the emulsified bromide, the two are well shaken up together, it is then poured out and set without further treatment, and washed in the usual manner. If the emulsion be kept for twelve hours before washing, it will be found to have great sensitiveness.

The success of this method in giving sensitiveness shows that the sensitive form of bromide formed by

ammonia is quickly arrived at in a but slightly viscous fluid, whereas it is not fully formed until a quarter to half-an-hour has elapsed (and even then not unless the solution be rendered less viscous by warming), when the full quantity of gelatine is employed. There is one thing that has struck us in using the emulsion, viz., the large number of plates that can be coated with this quantity of emulsion.

Henderson's Process.—Mr. Henderson has a modification of the cold emulsification process, which he published in August 1882; his formula is as follows:—"Here I have a solution of gelatine 10 grains dissolved in 1 ounce of water; when the gelatine is dissolved by gentle heat, I add ammonia carbonate 20 grains (the ammonia causes effervescence):—

| | | |
|----------------------|-----|------------|
| Bromide of potassium | ... | 150 grains |
| Iodide " " | ... | 2 " |
| Alcohol ... | ... | 3 ounces |
| Ammonia .880 | ... | 60 minims |

Mix ammonia and alcohol before adding to gelatine.

This may be kept in bulk, ready for use; it will keep a long time good. When it is quite cold, I stir in—

| | | |
|-------------------|-----|------------|
| Nitrate of silver | ... | 200 grains |
| Water | ... | 2 ounces |

I occasionally shake it, and in one hour it will be ripe enough for all ordinary purposes; in fact, when finished, it will give results twice as rapid as most commercial plates. The maximum sensitiveness seems to be reached in about ten hours. No further advantage is to be derived by prolonging the emulsification, except that of convenience.

It should be apparent that, to have a large reservoir of emulsion made in this way, to draw from daily, or at will, adding fresh to keep up the stock, perfect uniformity must be obtained.

To the above quantities I add 4 to 5 drams of dry gelatine, and warm gently to dissolve the same. When the gelatine is thoroughly dissolved, I stir in 12 ounces of warm methylated alcohol (100°). The emulsion, when cool, will precipitate on the bottom of the vessel; it is to be broken up and well washed in a running stream from two to twelve hours. Make up bulk to 8 or 10 ounces. Gelatine dissolved in alcohol, ammonia, and water, will not set so firmly as the same amount of gelatine in water; yet, if the salts and ammonia are removed by precipitating with excess of alcohol, the gelatine recovers its setting powers."

We have tried this plan of emulsion making at various times, and can say that it yields an excellent plate, and very sensitive. At the same time we are not prepared to give it such excellent qualities as is obtained by the boiling process. The drawback to it is the large amount of alcohol required to precipitate the emulsion, and its consequent cost.

CHAPTER XV.

MR. COTESWORTH'S COLD EMULSIFICATION WITHOUT AMMONIA.

Mr. COTESWORTH described a plan of gaining sensitiveness by allowing an emulsion to gain sensitiveness by remaining liquid at ordinary temperatures. We recollect that a somewhat similar proposal was made of emulsifying at a low temperature in gum-arabic. Following out Mr. Cotesworth's general directions, we have arrived at fairly satisfactory results. An emulsion is prepared, as far as the boiling operations, according to Chap. IX., the mode of mixing given at page 72 being preferred. An emulsion which has a beautiful ruby colour, if kept liquid, will, in twenty-four hours, have attained a grey-blue colour. A comparison with Bennett's process (Chapter X.) will show that the difference between the two processes is, that Mr. Cotesworth uses very little gelatine for emulsification to begin with, whilst Mr. Bennett uses the full quantity. The consequence is that the latter gentleman was obliged to have recourse to prolonged emulsification at about 95° , in order to overcome the viscosity of the gelatine, whilst the former can get sensitiveness in twenty-four hours at (say) 60° F.

In cold weather we have found it necessary to add a couple of ounces of water to the sensitizing emulsion, in order to prevent setting. In this case the extra gelatine required is added dry, and, after soaking, the emulsion is warmed, and the gelatine melts.

There is nothing different in the preparation or development of the plates to call for any special remark.

CHAPTER XVI.

A PROCESS FOR GELATINE EMULSION-MAKING IN HOT WEATHER.

THE formula adopted is precisely that given in Chap. IX., except that, before washing, 120 grains of autotype, or other hard gelatine, are kept back. After boiling, if this plan be adopted, or after using Cowan's cold emulsification (see Chap. XIV.), and adding 120 grains of gelatine in 1 oz. of water, the emulsion is poured out into a jam-pot, which is immediately placed in iced water with a few lumps of ice floating in it. In half-an-hour the gelatine will be firmly set. The gelatine is loosened from the sides of the jam-pot, and the lump of emulsion is transferred into moist canvas, and squeezed through into a jar of iced water (the water having been run through filter-paper to get rid of all floating matter) in which a few small lumps of washed ice are floating. After ten minutes the water is changed, and after another ten minutes is changed again, when it is again collected in the canvas, and squeezed through into water. One more change of water should be sufficient to free it from all except traces of soluble salts. It is then transferred to the canvas, and allowed to drain over a jar for half-an-hour to three-quarters. It is again transferred to the jam-pot and melted, and the remaining 120 grains of gelatine, which have been allowed to swell in about

three-quarters of an ounce of water, is added, together with two or three drops of carbolic acid (or other anti-septic), and then once more placed in iced water. In half-an-hour it is set, when it is covered with alcohol and allowed to ripen for a day; and if the jar be placed in water containing a lump of ice, so much the better. When plates have to be coated, the slab on which the plates have to be set is covered with small lumps of ice for half-an-hour, and if the slab be thick it is only very gradually cooled; but, on the other hand, it also but very gradually gets warmed again. During this time the emulsion is melted, six drachms of alcohol, one grain of chrome alum in one drachm of water, added, and filtered. When the plates are coated (after the slab has been dried from all water), it will be found that the film of emulsion will set in a couple of minutes, and that the slab remains cool enough to enable five or six batches of plates, each batch filling the slab, to be prepared; that is, supposing your slab to hold eight plates, you can coat forty to forty-eight without re-cooling the slab. The gas of the drying-box may be lighted immediately, and the drying of the plates will proceed rapidly, and they will not re-melt. If gelatine be once *well set*, it requires a high temperature to re-melt it; and the more the water is evaporated, the higher the temperature required. As the current of warmed air passes over the plates, the moisture is rapidly absorbed, and hence the drying can be effected with safety.

CHAPTER XVII.

GELATINO-BROMIDE EMULSION MADE BY PRECIPITATION WITHOUT THE PRESENCE OF GELATINE.

THE next emulsion is one described in the *Photographic News* by the writer. It is a method of preparing an emulsion by adding *washed* silver bromide to gelatine.

Let us suppose we are going to make up about 7 ounces of gelatine emulsion. Weigh out ammonium bromide, 140 grains (or its *equivalent* in zinc, potassium, or any other bromide), and dissolve in 20 ounces of water (not necessarily distilled water). Next weigh out 250 grains of silver nitrate, and dissolve in 6 ounces of water, and add 6 drachms of glycerine to it, and stir thoroughly with a glass rod. We prefer to put this mixture in a glass jar holding about 40 ounces (an empty French prune bottle would answer every purpose).

The bromide solution should now be added very cautiously. Take a 10-ounce measure, and fill it up to six ounces, or thereabouts, so that it is not too full, and gradually drop, little by little, the solution into the silver solution, stirring very thoroughly the whole time. A milky emulsion forms, and gets thicker and thicker till the whole bromide in the 20 ounces is added, though, of course, the fluid is *per se* thinner; a quarter of an

ounce of nitric acid is next added, and well stirred up. This addition is made to save any chance of fog, which might be caused by the excess of silver present. The reason of this has already been described in Chapter III.

This emulsification is better carried on in a dark room, though it is not absolutely necessary. *The bromide solution must be poured into the silver solution, and not vice versa, or a failure will be most probable.* The glass jar and its contents may now be placed away into a cupboard, and left for as long a time as is convenient, but not for less than a quarter of an hour. By the latter time the silver bromide will have fallen to the bottom of the jar, with the exception of a very *slight* milkiness, which will subside in a couple of hours. The silver bromide, however, left in suspension at the end of the quarter of an hour is so small that it may be decanted off without detriment to the emulsion. The jar may be tilted, and the liquid poured off, or a syphon may be introduced (and this is a neater way), and the liquid syphoned off close to the precipitate. About 20 ounces of water are again poured into the jar, the precipitate well stirred up, and again allowed to subside. As soon as ever the subsidence takes place, the water is again decanted or syphoned off. This operation is repeated four or five times, after which the decanted water may be tested for acidity, and for silver nitrate.

To try for the former, moistened litmus paper is held over an open ammonia bottle till it is thoroughly blue, then well washed in distilled water; this is thrown into the decanted water. The faintest trace of acid will redden it. If it does turn red, the washing must be repeated. To test for free silver nitrate, add to the wash water 1 drop of potassium chromate. A red colouration indicates the presence of silver nitrate. In case of the presence of

* It should be remembered that the wider the diameter of the jar, and the shallower the water, the greater will the precipitate collect at the bottom.

either one or the other, as is shown by the litmus paper and the chromate, the washing must be continued.

The original plan we adopted, and of which the above is a modification, consisted in precipitating silver bromide in pure water, and without the help of glycerine. This is still one of the best methods we have tried, and we give a *resume* here.

Weigh out the materials given on page 70, except the gelatine. Dissolve 1 and 2 in 4 ounces of water, and 4 in another 4 ounces of water. Take 20 ounces of water in a glass beaker and a stirring rod, and add to it first $\frac{1}{2}$ a drachm of the silver nitrate solution, and then, drop by drop, $\frac{1}{2}$ a drachm of the bromide solution, then another $\frac{1}{2}$ drachm of the silver solution, and another of the bromide solution, and so on, till the solutions are exhausted.

A still better plan is to have the solutions in pipettes on a stand, and allow each solution to drop into the water, stirring all the while.

The precipitate will be so fine that in some cases a couple of days will elapse before it subsides. It may be hastened by raising the water containing the precipitate to the boil. The particles then will coagulate together, but this does not signify, since if they have been precipitated in a fine state of division, they will separate again in subsequent operations. The washing takes place as above described.

The next part of the process has now to be taken in hand. 100 grains of gelatine are soaked in 2 ounces of water; this 100 grains should be Nelson's "No. 1 photographic gelatine," and another 100 grains of harder gelatine, such as Autotype or Swiss hard gelatine in 3 ounces of water. The No 1, when it is soaked, is taken up on a rod, and the vessel containing the precipitate is placed in hot water, and the gelatine used as a mop to collect it. The gelatine gradually melts, and the bromide becomes emulsified. It is then transferred to a flask, and heated in boiling water for five minutes, and well shaken up.

When the froth has subsided, the bottle is again shaken, and the warming process repeated. After two or three such shakings, a little of the gelatine emulsion may be dropped upon a glass plate, and examined for granularity. If absent, so much the better; but if present, half the second lot of the harder gelatine, which has meanwhile been dissolved, must be added, and the shaking repeated.

If the emulsion be raised to boiling (as at page 142) for five minutes, then shaken, and the same operation repeated a second time, we believe that an emulsion is obtained which, for rapidity, will bear comparison with any other process. This plan will give as smooth an emulsion as any other method, provided the operator's fingers are not all thumbs when the bromide is dropped into the silver.

When the emulsion is ready, the remainder of the gelatine solution not already added should be poured into the bottle, together with half an ounce of alcohol, and after a final shake, and filtering through washed cotton-wool, it is ready for coating the plate.

CHAPTER XVIII.

DR. VAN MONCKHOVEN'S PROCESSES.

1st Process.—Dr. Van Monckhoven, in trying the writer's original plan of washing the silver bromide before adding it to the gelatine, failed, but hit upon the following ingenious methods, which are given in his own words:—

“I prepare very pure and dilute hydrobromic acid, and I determine accurately the amount of it required to precipitate exactly 150 grains of silver nitrate. I then dissolve this quantity of acid in 7 ounces of water, with which I incorporate, by heating, 40 grains of gelatine. On the other part—and from this moment I entirely operate in the dark room—I precipitate 150 grains of silver nitrate by a very slight excess of bicarbonate of soda; I let it settle for twenty-four hours, and then renew the water to the same amount, after which I let it settle again previous to decanting. On this precipitate of silver carbonate I pour a hot solution of 30 grains of gelatine in 7 ounces of water. This is well stirred, and then I pour on it the solution of gelatine and hydrobromic acid. The mixture is thoroughly shaken every quarter of an hour, and is kept at the constant temperature of 120° Fahr. The silver carbonate dissolves slowly in the hydrobromic acid, and the silver bromide is formed in the colloidal liquid in a state of extreme sub-division. At the end of

ten or twelve hours the mixture, when flowed over glass plates, has a greenish white colour. I next introduce 150 grains of gelatine, cut into very thin shreds, which I dissolve by stirring, and then, without washing the emulsion, I flow it over the glass plate.

"In order to obtain a success with this method, it is necessary to take some precaution. The hydrobromic acid must be free from phosphorus and sulphur; the water used for washing the silver carbonate must contain no trace of carbonic acid.

"In an emulsion prepared by this method there is always an excess of hydrobromic acid and of silver carbonate, but I have satisfied myself by other experiments that the presence of these substances does not affect the results. This is not the case if carbonate be replaced by the oxide of silver; the emulsion is then grey, and gives rise to fogging. The plates that I have prepared by this method are twenty times as rapid as the best wet collodion, and, compared with the best English plates, I have found them to be three or four times as rapid. For the rest, the same observations and the same methods apply also to collodio-bromide."

2nd Process.—Dr. Van Monckhoven's second process is as follows :—

"Procure some of Nelson's No. 1 photographic gelatine. I insist upon this point, because you will not succeed with German or French gelatines, which are prepared in a different manner from those of Nelson. Weigh out exactly 153 grains of this gelatine, and 122 grains of pure and well-dried ammonium bromide. Put these two substances into a bottle, and pour upon them 10 ounces of distilled water. In a quarter of an hour the gelatine will have swollen, and you can now put the bottle into a warm water bath and agitate, in order to dissolve the two substances.

"Weigh out 184 grains of silver nitrate, and dissolve in $1\frac{3}{4}$ ounces of distilled water. Now pour the silver

emulsion into the bottle containing the bromide, a little at a time, well shaking it after every addition. When all the silver solution has been added, pour in 1 drachm of pure ammonia of a density of .880, and well shake up the solution. The ammonia exercises a special action here; its effect is to render the emulsion ready to be used in a few minutes, or, if great sensitiveness be required, it can be obtained in a few hours instead of days, and thus decomposition of the gelatine is avoided.

"Now pour the solution of gelatine into a porcelain dish, and place it upon cold water, and let it set. When set, detach it from the dish, place it in a strong linen sack, and wring it so that the gelatine is expelled in shreds, which are easily washed on a fine sieve. A washing of five hours in water three times changed suffices. Collect the pellicle on a clean linen cloth, and dissolve it at a temperature of 35° Centigrade, and it is fit for use. This process is a combination of those of Mr. Bennett and Messrs. Wratten and Wainwright, with this difference—that I add the ammonia in order to have the emulsion ready to work in a few hours instead of days."

CHAPTER XIX.

PREPARATION OF THE PLATES.

Cleaning the Plates.—A good emulsion is often condemned for frilling when the methods used in cleaning the glass plates are, in reality, at fault. It is our own practice to immerse the plates in nitric acid and water (1 to 10), then to wash, and next to rub them once with a 10 per cent. solution of caustic potash or soda and a little methylated spirit. After a wash under the tap the water should flow quite evenly from off them, when, after a rinse with distilled water, they may be set up to dry, which they will do very rapidly if allowed to stand on clean blotting-paper. Polishing a plate is a mistake; it only encourages the formation of blisters, as it prevents the adhesion of the film to the glass. Avoid French chalk, or anything but pure water, and then one of the causes of frilling and blistering will have been eradicated. The plates having been cleaned as above, they are brought into the dark room, which should, if possible, be kept at a temperature between 50° and 65° , as this is the heat which is most convenient at which to coat the plates and to ensure setting.

Substrata.—With emulsions made with certain kinds of gelatine, the tendency to frill is not easily overcome, in which case it is necessary to coat the plates with a

substratum of some sort. The following is one formula (Mr. Forrest's) which may be used:—

| | | | | |
|-------------------|-----|-----|-----|-----------|
| White of egg | ... | ... | ... | 1 ounce |
| Water | ... | ... | ... | 20 ounces |
| Methylated spirit | ... | ... | ... | 1 ounce |
| Carbolic acid | ... | ... | ... | 20 drops |

The carbolic acid is added with stirring to the spirit, and then the mixture is poured into the albumen and water, which has been previously mixed.

Dr. Vogel gives another substratum, which is also efficacious and easily applied:—

I.

| | | | | |
|-------------|-----|-----|-----|---------------------|
| Gelatine | ... | ... | ... | 50 grains |
| Acetic acid | ... | ... | ... | $\frac{1}{2}$ ounce |

are placed in a bottle and warmed till solution takes place. This keeps a month.

II.

| | | | | |
|-------------|-----|-----|-----|---------------------|
| Chrome alum | ... | ... | ... | 10 grains |
| Water | ... | ... | ... | $\frac{1}{2}$ ounce |

is next prepared.

| | | | | |
|-------------------|-----|-----|-----|----------------------|
| Take of No. I | ... | ... | ... | $2\frac{1}{2}$ parts |
| No. II | ... | ... | ... | 1 part |
| Methylated spirit | ... | ... | ... | 70 parts |

and filter; coat the plates, after cleaning and drying, as with collodion, and allow the substratum to dry.

The late Mr. Henry Cooper introduced a gelatine substratum, the preparation and application of which he describes as follows:—

“Soak 60 grains of Nelson's photographic gelatine in water, drain, and pour on enough boiling water to make 8 fluid ounces. Now add 2 drachms of a ten-grain solution of chrome alum, and stir vigorously for a minute or two. Filter the solution through paper into a clean measure, keeping it warm and avoiding air-bubbles.

“To save trouble, a large quantity of each of the solutions, the gelatine and the chrome alum, may be prepared, and will keep for a long time if a little pure carbolic acid be added to each. No more must be mixed than is required for the batch of plates, as when the compound solution has once become cold, it cannot be again liquefied with heat. The measure and filter used must be well washed with warm water as soon as done with, for the same reason.”

Levelling Shelf.—The next point to look to is the shelf on which to lay the plates after coating. In our own practice, we have a piece of thick plate glass about 3 feet long by 1 foot broad, and $\frac{3}{4}$ -inch thick.* We level by means of three mahogany wedges and an ordinary spirit level.

The level L is placed first across the plate, and the two wedges X and Y are altered till the bubble B of the level is

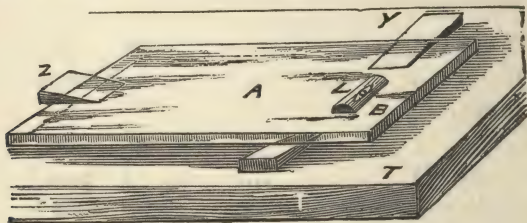


Fig. 16.

central; the level is then turned lengthways along the plate, and the bubble caused to occupy its proper position by shifting Z, not touching X or Y. This should cause the plate, if true, to be accurately level; but it is as well to repeat the operation. A couple of supplementary wedges are sometimes useful if the glass “spring” at all.

Level Cupboard-shelves.—Instead of a levelling shelf as given above, it is perfectly feasible to alter the cupboard

* A ground slate slab answers equally well.

shown at page 22, and the alteration does away with the drying markings sometimes found, and due to the iron wires. The wires are removed, and glass or slate strips substituted for them. For plates $8\frac{1}{2}$ by $6\frac{1}{2}$, slips 3 inches wide are sufficient, and they should be a $\frac{1}{4}$ -inch thick to prevent bending. One end of the slip is supported in a stirrup shown in fig. 17, in the top of which is a slot,

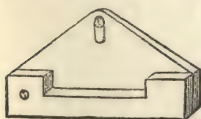


Fig. 17.



Fig. 18.

through which a screw is passed into the cupboard; opposite to this is another stirrup (fig. 18), into which are inserted two thumbscrews as shown. This is placed exactly opposite the first stirrup in the cupboard. The strip is placed between these two stirrups, and is first levelled crossways by means of the thumbscrews. When level in this direction the length of the strip is levelled by raising or lowering the first stirrup, and when in position the screw in the slot is screwed home. When once levelled, the strip will always fall level into position. In our own cupboard we have seven of such strips across the cupboard, and they answer admirably. The coated plates are at once placed on these shelves, and allowed to set in the position in which they are to be dried.

It has been stated (though we have never found it so) that markings may be met with owing to the emulsion setting more rapidly in those parts of the plate which are in contact with the strips. If such should be feared, we recommend that triangular pieces of card of $3\frac{1}{2}$ inches size should be cut, and drawing-pins passed through them at each corner, and that these, with points uppermost, should be laid on the strips where the plates have to be placed. The setting will then take place without any chance of drying markings, since the plate will be

supported by points. Drawing pins may be got by the gross, all of the same height. This plan is very suitable for warm weather when plates take long to set, as a levelling shelf in such weather often becomes filled before the plates are sufficiently set to be moved to the drying cupboard.

Some dry-plate makers prefer to dry their plates in a nearly vertical position in racks, and there is no doubt that when drying takes place in this manner there is less chance of dust settling on the plates (see page 34).

Coating the Plate.—The emulsion, having been filtered, is kept in a jar at a temperature of about 90° F. by means of a hot-water bath. It should be tested for its flowing qualities; *i. e.*, whether it has enough alcohol, and whether it is thin enough. It is hard to describe when an emulsion is of exactly the right consistency. It should flow like oil; and, when the plate is drained by tilting, a thin film of emulsion should be left. As a rule, the emulsion, during washing at about 60° F., will have taken up just enough water, whilst at 20° lower, perhaps a drachm to the ounce of water will have to be added; and at 70° it is probable that about 15 per cent. of dry gelatine may have to be added. To coat a plate by hand, a plate is taken on a pneumatic holder, or held upon the tips of the fingers. We will suppose the plate is of the 6½ by 8½ size that is to be coated. About 2 ounces of emulsion are poured into a warmed measure,* *taking care that no bubbles are formed* (which can be secured by pouring out the emulsion against the side of the measure), and a pool of gelatine is made at the top of the plate. It is then, by careful pouring, made to fill up the centre of the plate, and flow to the right-hand top-corner, next to the left-hand top corner, then to the left-hand bottom corner, and, finally, to the

* Small emulsion pourers are now to be had. They are like small teapots, with an inner pot into which the emulsion is poured. The emulsion used to cover the plate is thus taken from the bottom of the bulk; and bubbles which may be on the surface are thus avoided.

right-hand bottom corner, where it can be partially poured back into the measure. The amount used should be noted; about three drachms should be sufficient to well cover the plate. The plate is then detached from the pneumatic holder (if used), held by the two corners of the diagonal, and quietly rocked till an even coating is seen to be secured. It is then cautiously slipped on the level shelf, and left to set. Another plate is taken and similarly treated; and when the shelf is full, the emulsion on the first plate will have set, and it must be removed to the drying-box or cupboard. This operation, when the operator is an adept at it, can be very rapidly performed. A quick coater will coat 150 $8\frac{1}{2}$ by $6\frac{1}{2}$ plates in an hour with ease.

There are other modes of coating the plate to which we may refer. After a central pool is formed on the plate as above, the emulsion may be guided by a glass rod along each edge, and thus the chance of spilling is lessened. For our own part, we think that this is not a good plan; first, because the glass rod is liable to collect dust, as it must be wiped between the coating of every plate; and secondly, if the central pool of emulsion be not spread out rapidly, coating marks are apt to be seen on the finished negative.

Another plan which is advocated is to brush the plate over with a very thin film of emulsion by means of a wide badger-hair brush (kept in a small quantity of warm liquid emulsion), and then to pour over the plate the full quantity. This is not a bad plan if the brush be kept clean. If resort must be had to any aids, our preference is rather to use a ruler or squeegee, somewhat longer than the plate, and covered with swans-down calico. This should be moistened with clean water and swept along the surface of the plate, and then the emulsion poured on immediately afterwards. *With plates to which a substratum is given*, some such artifice is necessary, since the emulsion invariably drags.

If any quantity of plates is to be prepared, it may be advisable to use a coating machine, which, for its principal parts, consists of a very finely turned india-rubber roller, A, and a trough, C, in which the roller works (fig. 19). The trough is filled with emulsion, which is

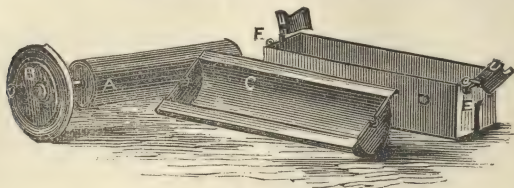


Fig. 19.

kept warm by a water jacket, D, below it. This in its turn is kept warm by a small gas jet or by a spirit lamp. The roller turns on its axis in slots, E E, in the water jacket, is made to revolve by a grooved wheel, B, about twice or three times a second, either by connecting B with a water motor, or by turning by hand, the movement being towards the operator, by which means it is covered with a uniform coating of emulsion. A plate is taken on a pneumatic holder, and the plate made to pass rapidly over the top of the roller, and is immediately turned with the coated side up, and rocked to give an even surface. It is then placed on a slab to set.

Drying the Plates.—Should a room be available which can be darkened, and in which the passage leading from the door can be darkened, there is nothing better than this for drying plates. It is well, however, to provide for a constant change in the air by means of an inlet tube on the principle of Tobin's ventilators, and an exit tube. A small coil of water pipes in a small room will much aid the change of the air; and, in fact, some such artifice must be adopted when many plates have to be dried. The plates may be racked in some such racks as given at page 34. Great care should be taken against dust. A boarded floor

is not safe; kamptulicon should be laid down, and, if practicable, the walls and ceiling should be papered with a well-varnished paper. This enables all parts of the room to be washed down, and so to be deprived of any adherent dust. Should a room not be available, then resort must be had to a drying cupboard, such as described in Chapter V.

The temperature of the cupboard should be kept as even as possible, sudden changes being detrimental—producing markings. Opening the drying cupboard door before the plates are dry, when once the gas has been turned on, is a mistake; the plates should be left until it is judged they are quite dry. Very quick drying is a mistake, as the different layers of the film get an uneven strain, and cause frilling. Six hours is about the minimum time which we can recommend, unless drying by alcohol is resorted to. The temperature should, if possible, not exceed 80° F., and the gas must be regulated accordingly. Drying by alcohol is effected by placing each plate, *after thorough setting*, in a dish of methylated spirit free from resinous matter for ten minutes, when it will dry in an hour without difficulty.

CHAPTER XX.

TESTING PLATES.

ALL plates, whether commercial or otherwise, should be tested before a batch is taken into use. We have often found plates blamed simply because such testing has not been carried out. Plates should be tested (1st) for speed, (2nd) for brightness, (3rd) for density giving qualities, (4th) for frilling and other imperfections.

Testing for Speed.—In our own practice we always test plates by means of one of Warnerke's standard sensitometers, but anyone may make a sensitometer for himself

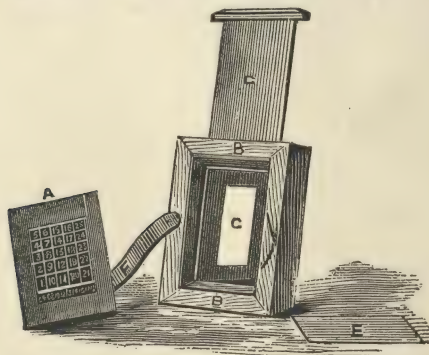


Fig 20.

which will be sufficient. Warnerke's sensitometer consists of a plate A, marked out into small rectangles of different opacities. These opacities are so arranged that each

succeeding space is just $\frac{1}{3}$ more opaque to white light than the one immediately before it. They are numbered in distinct numbers in the order of opacity. This mask is placed in a pressure frame, B, in front of which, and fitting into a groove, is a phosphorescent plate, E, which is placed behind C. The light of this can be made to pass through the sensitometer screen on to a gelatine plate in contact with it, by withdrawing a shutter (shown open in the figure). To use this instrument, the phosphorescent plate is excited by an inch of burning magnesium wire held close to the surface of the plate. It is then placed in the groove cut for it, the illuminated surface being towards the shutter. Between exciting the phosphorescent surface and the exposure of the plate to its action exactly a minute is allowed to lapse. The shutter is then withdrawn, and the plate receives the light through the screen for *half a minute*, when the shutter is closed, and the plate is developed. The last figure which can be read after fixing the plate is the "sensitometer number" of that plate. The following table, compiled by Mr. Cadet, can then be used to compare the sensitiveness of one plate with another:—

| | | | Number of times more sensitive than | | | | | | | | | | | | | | |
|----|-----|-----|-------------------------------------|----|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | | | { | 25 | 24 | 23 | 22 | 21 | 20 | 19 | 18 | 17 | 16 | 15 | } | | |
| 25 | ... | ... | ... | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ | 3 | 4 | 5 | 7 | 9 | 12 | 16 | | | |
| 24 | ... | ... | ... | | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ | 3 | 4 | 5 | 7 | 9 | 12 | | | |
| 23 | ... | ... | ... | | | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ | 3 | 4 | 5 | 7 | 9 | | | |
| 22 | ... | ... | ... | | | | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ | 3 | 4 | 5 | 7 | | | |
| 21 | ... | ... | ... | | | | | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ | 3 | 4 | 5 | | | |
| 20 | ... | ... | ... | | | | | | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ | 3 | 4 | | | |
| 19 | ... | ... | ... | | | | | | | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ | 3 | | | |
| 18 | ... | ... | ... | | | | | | | | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ | 3 | | |
| 17 | ... | ... | ... | | | | | | | | | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ | 3 | |
| 16 | ... | ... | ... | | | | | | | | | | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ | 3 |
| 15 | ... | ... | ... | | | | | | | | | | | 1 | $1\frac{1}{3}$ | $1\frac{3}{4}$ | $2\frac{1}{3}$ |

The numbers down to 15 only are given, this being more than sufficient for comparison of most plates. Supposing it is desired to compare the rapidity of two plates showing different numbers, look for the higher number in the column on the left side of the table, and the lower one in

the top horizontal row of numbers, then run the eye along the line of the number in the left-hand column until you come to the figure under the lower number; the figure will then show the number of times more sensitive is the plate showing the higher number than the plate showing the lower number. For instance, a plate showing 21 is four times more sensitive than one showing 16; one showing 20 is three times more sensitive than one showing 16, and so on. In both cases the development should be by a developer which is suitable to the plates. A good standard developer will be found in the chapter on Development. It is sometimes doubted, though we believe incorrectly, that the sensitometer results are not in accordance with those given by the camera. For our own part, we do not believe in any great discordance, though it is possible that there should be a slight one. If any doubt exist in the mind, a plate of known sensitiveness may be placed in one half of a dark slide, and the plate whose sensitiveness has to be judged in the other, and an exposure made in the camera. It is then easy to tell at a glance which is the better exposed picture.

Testing for Brightness.—The brightness is ascertained readily by examining the plates already tested in the sensitometer. In case a sensitometer is not at hand, it is a good plan to expose a plate in the camera; pull out but half of the front of the slide. On development, the least trace of fog (green or grey) is seen on the unexposed parts.

Testing for Density.—It is unfair to test for the density-giving qualities of a plate by exposure in the camera unless the light is bright. Our own practice is to use a dense negative, from which a transparency is taken with the plate to be tested. A good exposure is given by passing a lighted match over the surface of the negative, which is in a pressure frame with the plate in contact with it. In the positive, after development and fixing, the deepest shadows of the picture should be sufficiently opaque to very greatly dim the light from a candle

flame when looked at through the densest portions. If a long exposure and plenty of restraining bromide be used, most plates will give good density on fixing if the plate be not starved of the sensitive salt of silver. When a plate is looked at by reflected light before exposure, a finger pressed against the back should not be visible. If this be the case the plate has not been sparingly coated.

Testing for Frilling, &c.—We have already stated (page 46) how dull spots which give opaque spots on development can be distinguished on a gelatine plate—viz., by shining the plate to the light coming from a gas flame through stained red glass. The spots, of course, can be seen on development, and need not be remarked upon further.

Plates which frill, usually do so after withdrawal from the hyposulphite bath, and on immersion in the wash water. The reason of this is due to the property that gelatine has of allowing pure water to diffuse through a layer of gelatine more rapidly than a salt solution will diffuse out. The cure for this is to use a second bath of weak hyposulphite, or even of common salt, and then wash the plate. Plates with a substratum on them rarely blister or frill. If plates frill with the developer made alkaline with ammonia, the plates should be tried with the developer made alkaline with carbonate of potash or carbonate of soda. If the tendency to frill or blister with ammonia be slight, these last developers should give immunity from it. In every case of a tendency to frill, the plate, before fixing, *should be immersed in the alum bath* for five minutes.

Our advice, however, if plates frill or blister, is to reject the batch, and make or buy others, as it will save disappointment.

In conclusion, we would earnestly recommend any photographer not to rely on any plates without previously testing them. The trouble is small, as is the expense, but the worry and annoyance of unsuccessful negatives

due to this cause are great. There are excellent plates in the market, but they vary in their quality and rapidity at times, as is almost inevitable. The manufacturers may have the most perfect machinery and chemical appliances, but as plates are dependent for their excellence to a great extent on the quality of gelatine employed, and as no two samples of gelatine are absolutely alike in composition, and on no two days is the temperature exactly alike, it can be well understood that such variations are almost certain to occur.

There is one defect which arises in negatives, to which special allusion is here made, viz., small pinholes in the densest parts—generally in the sky. The plates are usually blamed for these, but in the majority of cases it will be found that they are *due to dust* (see next chapter).

CHAPTER XXI.

EXPOSURE OF THE PLATES.

WHETHER the plate be made at home, or bought, there are certain necessary precautions to take when exposing it in the camera.

Examination of Slides.—The first thing to be done is to examine the dark slides, and this should not be done in a casual manner, but should be done thoroughly before they are filled. The greatest enemy to clean work is dust in the slides, and much care should be taken in searching for it, and for getting rid of it. In the fronts of the slides the rabates should be carefully passed over with a bristle brush, and the woodwork and separating partition of the double back should be equally well dusted. If a journey is contemplated, it is well to pass a rag moistened with glycerine over the rabates, and, in fact, over the inside of the whole of the slides, to act as a dust trap. Of course but a very slight film of glycerine should be left, but the faintest trace is sufficient to catch any fine dust that may enter. For better security, too, of the plates, the slides should be tied up in bags (thin waterproof sheeting is a good material of which to make them). The plates themselves should each be dusted with a badger hair brush, and, if practicable, each one should be shined by reflected light, and viewed by transmitted light, to make certain

that no surface imperfections, such as dull spots, are on the plates, and that the plate has been uniformly coated, and has no pits or other markings which would spoil a negative. No one who has not practically proved it, can be aware of the disappointment that is caused by taking a negative on such a plate which, if the blemishes caused by such imperfections were absent, might be ranked as a perfect one.

Focussing the Picture.—It is beyond the scope of this work to teach the artistic side of photography, and for it a reference should be made to such works as "Pictorial Effect in Photography," or "Picture Making by Photography."* We will suppose, however, that a landscape has been chosen, that the lens is a good one, and that the camera is not one of those rickety articles which may be described as cheap and nasty. We will, moreover, suppose that the legs are light, and yet firm; and that the base of the camera fits tightly on them. In the days of wet plate photography the rule to be followed was to focus with the largest stop that would give passable definition. In these days of rapid plates the rule is to use a small stop, so as to enable the exposure to be slightly prolonged. When the writer focusses a picture, he uses the largest stop, which gives decent definition, and before exposing the plate alters it to a stop of half that diameter, or nearly so. By this means the sharpest definition is got, and the resulting negative is one which will bear enlargement if necessary. Some landscape photographers make it a point to use the smallest stop of their lenses in all cases. If they err, they err on the right side. As a rule, every lens has some stop which, when used, gives the crispest, and yet sharp image. With instantaneous pictures the largest stop consistent with fair definition should be used, particularly if the plates are not exceeding rapid. With plates that register 24 on the

* By H. P. Robinson (Piper and Carter).

Warnerke sensitometer, No. 4 stop, or $\frac{f}{30}$ of a "rapid rectilinear" lens, should admit sufficient light to obtain a picture in the $\frac{1}{10}$ of a second if the light be good, and if the views be tolerably open.

It may not be out of place to give a few general remarks as to the methods of "placing" the picture on the focussing screen when photographing a landscape picture. First of all, if the principal object is a building, a doublet combination of lenses should be used, in order that the lines may be straight, and not curved, which is the case when a single lens is used. Then care should be taken that the top and bottom of the focussing screen are parallel to the horizon. This can best be ascertained by using a small level. Now, if the building is a high one, the camera may have to be tilted so as to include the whole, in which case care should be taken to use the swing back (with which every camera should be provided), so that the focussing screen is vertical (plumb). This ensures that the vertical lines of a building, besides being straight, will also be parallel, a point which is insisted upon in proper perspective. When this is done, then insert a stop, and focus the image as sharply as possible.*

Note if the sun be shining into the lens, and if it is, carefully shade it. (There are sky shades supplied with cameras now which are very useful.) Be particular to focus sharply the object which is to be the "nucleus" of the picture, and note whether any improvement can be made by a shift in position of the camera. For a pure landscape, if a building be not in the margin of the focussing screen, a single lens may be used, as any small curvature to straight lines which may be given will not be perceptible. Focus the principal object sharply, and if a large stop has to be employed owing to want of light or a required rapidity in exposure, the slight want of sharp-

* If the swing-back be used, it will be found that a smaller stop will have to be used than if the focussing screen is in its ordinary position.

ness in the remaining portions will not tell much against the picture.

One more word: never take a picture without some principal object in it; every good composition should have some point of prime interest, and the lines and general sweep of light and shade should lead up to it. One object of interest in a picture is better than a dozen, as then the eye is not distracted, but can dwell on it and remember it.

Exposure in the Camera.—When gelatine plates are used, there is an addition to the camera which well repays the preliminary cost, when comfort and ease of exposure are taken into consideration; we allude to the use of a shutter worked by a pneumatic arrangement, by which any desired exposure can be given. At the risk of being told that we are advertising a particular article, we honestly say that one of Cadett's shutters, which works inside the camera and at the back of the lens, is that one which fulfils the object in view better than any other with which we are acquainted. With it exposures can be given from any number of seconds to about the $\frac{1}{6}$ of a second by merely pressing the ball of the pneumatic arrangement. This prevents any shake that might be given to the camera at the moment of uncapping the lens, a point of very practical importance when the exposure is short. We will suppose that the camera is provided with some such arrangement, or with a substitute for it. When the box containing the slides is opened, direct sunlight should not be allowed to play upon them, but they should be kept in the shade; for no matter how carefully a slide is made, it frequently happens that a gleam of sunlight is able to penetrate by reflection through some apparently light-tight crevice to the plate, causing a marking. The slide should be immediately covered with the focussing-cloth, and whilst so protected placed in the camera, where it should remain covered up. It is here presumed that before taking out the camera it has been thoroughly examined in bright light to see that

there are no pin-holes in the bellows; that the interior is of a dull black; and that the aperture of the lens in which the diaphragm is placed has been provided with a covering to prevent light penetrating to the plate by reflection when the front of the slide is withdrawn previously ready for giving the exposure. We may remark that a pneumatic shutter placed behind the lens (as we have suggested it should be in our ideal camera) lessens any danger of fog from this cause, as the light from the stop will only act during the time of exposure, and would probably not hurt the picture. It is far different, however, with a shutter in front of the lens, or where a cap is used; in these cases, from the moment the slide is drawn the fogging action of such light commences. A good protection to the Waterhouse diaphragm is an india-rubber band, whilst to rotating stops a cover is almost a necessity.

Now as to the time of exposing a plate it is impossible to say very much, since all depends on the rapidity of the plate; but this ought to be known to the operator by previous trial, and then a keen judgment as to the intensity of light in which the exposure is to be made ought to enable him to give an exposure not far wrong, at all events. In any case, it is better to over-expose than to under-expose; and with iodo-bromide plates, such as given in Chapter IX., six times, or even more, exposure than is absolutely necessary to give a perfect picture, is better than giving even one-third too little. In developing such over-exposed plates, a proper gradation can readily be obtained; whilst with an under-exposed plate, nothing can make it better than bad. Violent contrasts are the most difficult to manage properly. Thus, a snow mountain in sunlight in one part of the picture, with dark fir trees in shade in another part, are objects which not only try the expertness of the operator in development, but are extraordinary tests for the quality of the plates. It may be said that a thinly-coated plate should never be chosen for such a subject, but rather a

plate which is thickly coated. In the latter, the reversed action caused by prolonged exposure, though extant on the surface, may not reach the layers of gelatine emulsion next the glass surface. Any how, in every case it is necessary to time the exposure so that in no part of the deepest shadows is there any large amount of bare glass. The golden rule, then, is to give sufficient exposure, and to regulate the developer so as to correct any over-exposure.

When the plate is to be exposed, the front of the slide should be withdrawn, whilst the focussing cloth covers the whole of the back of the camera. It is absolutely necessary that all danger of light entering the slide be avoided by taking this precaution. The cloth should remain over the camera whilst the exposure is made. It is an excellent plan to have an elastic loop attached to the focussing-cloth to fit over the lens, and thus to prevent any slipping of the latter.

Exposure of Instantaneous Pictures.—A picture is said to be instantaneously taken when the exposure is very short, and to obtain these short exposures some kind of instantaneous shutter should be employed. There are many in the market, many of which are good. All are dangerous, however, if the camera is not very rigid, or unless they are detached from absolute contact with the lens. This may be effected by using a velvet bag to connect the opening in the shutter with the hood of the lens. If an instantaneous shutter is to be used, we like a drop-shutter form in its simplest form. Some shutters act as diaphragms to the lenses, and thus the *full* value of the exposure is not gained, as much as half the light being lost. The theoretical form that a shutter should take is that the full aperture of the lens should be exposed for as comparatively long a period as possible, whilst the uncovering and covering should take place as rapidly as possible. With this in view, the writer designed a shutter shown in fig. 21. C is the aperture for the lens; P, the

pin to which an elastic band, E, is attached; T, the releasing catch. In this we have a long drop shutter, the velocity of drop being augmented by an elastic band. With an opening of five inches an exposure of about one-

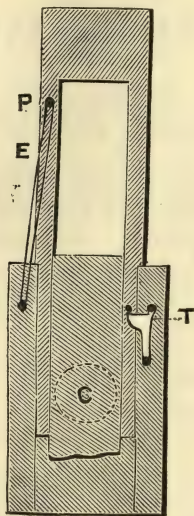


Fig. 21.

fifteenths of a second can be given. The shutter is attached to the lens by a velvet bag carrying an elastic ring, and, at the moment of exposure, is held by the hand. For ordinary rapid exposures, we like the flap shutter behind the lens, which we have alluded to.

Withdrawing the Slide.—The same precautions should be taken in withdrawing the slide as were taken in placing it in the camera.

CHAPTER XXII.

DEVELOPMENT OF GELATINE PLATES WITH ALKALINE DEVELOPERS.

IN Chapter II. we have already shown the theory on which development proceeds; but here we must enter a little more fully into the matter. We have shown, when the alkaline developer is used, that, *as a rule*, a restrainer, in the shape of soluble bromide, to prevent the primary reduction of the silver bromide unaltered by light, is requisite. We have italicized "*as a rule*," since, in some cases, this restrainer, which acts chemically, is really unnecessary, as a restrainer which acts physically can take its place. This was the case in the old albumen beer process, which was well known till emulsion superseded it; the iodide in the plate separates the particles of bromide one from the other, and the albumen wraps these up, as it were, in a colloidal sheath, through which the solution finds its way more slowly than it would if they were unshrouded. Gelatine is also a colloidal body, and we may expect to find the same hold good; as a fact, with many plates it does, and more especially with those plates which are prepared with an emulsion containing a large proportion of gelatine,* as compared to silver bromide.

* If we take emulsion, for instance, prepared by Bennett's process, we find that the proportion of silver nitrate to gelatine is 11 to 20; in the formula we have given at page 139 it is 20 to 16; that is, in one case the silver nitrate is about $\frac{1}{2}$ the weight of gelatine, and in the other $\frac{2}{3}$ ths. It can thus be easily understood how in one case no potassium bromide is required, whilst in the other a little is requisite.

With some commercial plates, for instance, where the silver bromide is minimized, alkaline development may proceed with the greatest ease without any chemical restrainer, the physical action of the gelatine being sufficient. It is for this reason that it is difficult to give any definite formula which can apply to all plates. In alkaline development, we may take it that there are three components: 1, pyrogalllic acid; 2, the alkali (usually ammonia); 3, the restrainer (usually potassium bromide). There are developers made with the carbonates of potassium and sodium, instead of ammonia. These are ordinary carbonates with an additional atom of the alkali tacked on them. It appears that it is these tacked-on atoms which is the active ingredient of the developer when combined with pyrogalllic acid, the carbonate being actually a restrainer. This may be proved by a simple experiment of using with an ammonia developer bi-carbonate of soda instead of potassium bromide, when the restraining action of the former will be seen.

Let us consider the different functions of the pyrogalllic acid, the alkali, and the restrainer.

The alkali and the pyrogalllic acid we will take first. As already pointed out (p. 15), pyrogalllic acid combines with the oxygen, and the bromine from the reduced silver bromide combines with the alkali. Suppose we have just sufficient of both to complete the reaction indicated, what will be the effect of increasing the one or the other?

If the alkali be increased we shall have a more rapid absorption of oxygen by the pyrogalllic acid. The oxygen may be obtained from the air, or from the alkali by the act of developing the image; we may conclude that the two sources from whence the oxygen is obtained will be used fairly equally. Hence, increase in amount of alkali means increased rapidity of development. But at the same time, *in cases of over-exposure*, it means that the effect of even a faint action of light is taken cognisance of at once, and the image becomes flat. Moreover, in

cases of extreme over-exposure, a large proportion of alkali means a reversal of parts of the image, which can often be avoided by using a weak developer, and consequently slow development. The developer can de-oxidize the oxidized molecules which cause the reversal before they are required to aid in building up the image. With a properly exposed picture more alkali gives an increased amount of reduced silver, which may increase density, since the pyrogallic acid will be used up to the greatest extent possible. It will also be seen that the addition of successive doses of alkali to the developer will give the same result when the exposure is correct; but vastly different if the exposure is too long.

The addition of pyrogallic acid to the normal solutions means an increased power of reduction and a larger amount of oxygen to be absorbed, and consequently more silver to be reduced; but it will be reduced more slowly than where the ammonia is in excess. Now slow development, in a properly permeable plate, means density in the high lights. It must also not be forgotten that pyrogallic acid is *per se* an absorbent of bromine when it has no oxygen to absorb.

In an $8\frac{1}{2}$ by $6\frac{1}{2}$ plate, on an average, about 8 grs. of silver bromide are reduced to the metallic state, and from this about $3\frac{1}{2}$ grains of ammonium bromide would be formed. Taking an ammonia developer, a little calculation will show that the presence of 2 minims of strong ammonia are necessary to cause this conversion in the presence of pyrogallic acid; and allowing for loss by vapourizing, at least 4 minims should be employed. The amount of pyrogallic acid to effect the same may probably be placed at about 2 grains, and allowing for oxidation, by contact with the air, 4 grains at least would be necessary for the full amount of ammonia. The bromide of potassium, or other chemical restrainer, slows the development, probably through a formation of a double salt of bromide of silver and potassium, which being reduced with difficulty

retards reduction, and hence a greater apparent density of deposit is given through the slower development.

Which of the Ingredients of a Developer should be first applied?—The question arises, should the pyrogallic acid, the restrainer, the alkali, or a mixture of all three, be *first* applied to the film? We believe that the application of pyrogallic acid first has a slight tendency to slow the plate; but, on the other hand, it is safe to do so, and then subsequently to add the other solutions together, little by little, till proper density is obtained. There can be no doubt that flooding the plate with a bromide solution first, is wrong in principle, since bromide has a tendency to destroy the photographic image; but with a carbonate this is not the case. On the other hand, a first soaking with a solution of the alkali, even in conjunction with a restrainer (which does not destroy the image), has much to recommend it, as pointed out by Colonel Wortley. When ammonia is used, it takes a minute quantity of silver bromide into solution, which, on the addition of pyrogallic acid (and bromide if necessary), is ready to be deposited on the image, and at the same time the reduction of the photographic image of sub-bromide to the metallic state commences. A safe plan, perhaps, is to flood the plate first with ammonia and bromide, or with an alkali, such as the carbonate of soda, and then to add the pyrogallic acid. But on the whole, for a properly exposed plate, we should recommend that all three ingredients should be applied at once to the film, but not of necessity in the full proportions. Wetting the plate before development is equivalent to diluting the developer, and, as a rule, is not to be recommended except in cases where there is a very horny film which requires softening, and then a slightly more concentrated developer should be used.

Development of a gelatine plate is in reality an art and science combined. The art consists in getting proper gradation, and the science in mixing your solutions to obtain it. There are only two kinds of exposed plates

which deserve attention at all: one when it is exactly timed rightly, and the other when it is over-exposed. An under-exposed picture should be washed off as quickly as possible, or else framed to illustrate a "horrid example."

Before accepting what has been laid down, the reader is strongly recommended to make a few experiments himself. First let him take formulæ such as the following:—

| | | | |
|-----------------------|-----|-----|-----------|
| P.—Pyrogallic acid... | ... | ... | 50 grains |
| Water ... | ... | ... | 1 ounce |
| B.—Potassium bromide | ... | ... | 50 grains |
| Water ... | ... | ... | 1 ounce |
| A.—Ammonia .880 ... | ... | ... | 2 drachms |
| Water ... | ... | ... | 2½ ounces |

These nearly correspond to 10 per cent. solutions.

Expose an $8\frac{1}{2}$ by $6\frac{1}{2}$ plate, and cut it by the diamond into six parts. Obtain a small dipping bath such as is used for quarter-plates, or a glass cell such as is used in physical laboratories.

The first experiment, perhaps, would be to take 20 minims of P, and add to it 1 ounce of water, place it in the dipping bath, and then immerse the end of one of the pieces of the plate in it for one to two minutes. Take it out and pour the pyrogallic acid solution into the cup, in which have been dropped 40 minims of B and 80 of A. Develop the plate in the dish, and note the result.

Other experiments of the same type are, to use the bromide first, then the bromide and the ammonia, and then the ammonia alone. Further experiments should then be made by increasing or diminishing the proportions of the pyrogallic acid, &c., when no doubt the reader will be able to confirm what has been said of the matter, or to make his own deductions.

Practical Development of a Plate.—The writer adopts the following method of developing plates, and which he has

found applicable to any he has tried. The following are prepared :—

| | | | |
|----------------------|-----|-----|-----------|
| 1.—Pyrogallic acid | ... | ... | dry |
| 2.—Potassium bromide | ... | ... | 10 grains |
| Water | ... | ... | 1 ounce |
| 3.—Ammonia .880 | ... | ... | 2 drachms |
| Water | ... | ... | 18 „ |

If a plate has received good exposure, the following is made up :—

| | | | | |
|-------|-----|-----|-----|----------|
| No. 1 | ... | ... | ... | 3 grains |
|-------|-----|-----|-----|----------|

(which is measured out by taking the amount on a slip of glass)

| | | | | |
|----------------------|-----|-----|-----|-----------------|
| No. 2 | ... | ... | ... | 2 drachms |
| No. 3 | ... | ... | ... | $\frac{1}{2}$ „ |
| Water, to make up to | ... | ... | ... | 2 ounces |

This is flowed over the plate, and the appearance of the outline is carefully watched; if it appears before 15 seconds, the plate is rinsed in water, and 2 more drachms of No. 2 are added, and development continued. This checks the rapidity of development, and allows sufficient density to be attained before the deepest shadows are at all dimmed. If the plate begins to develop in fifteen seconds, the action of the developer is allowed to continue till such time as the action begins to flag, when another $\frac{1}{2}$ drachm of No. 3 may be added; or, if the developer be very muddy, a fresh solution is employed after rinsing the plate.

Suppose the picture does not commence after (say) twenty seconds, this developer is made up :—

| | | | | |
|-------|-----|-----|-----|----------|
| Pyro | ... | ... | ... | 3 grains |
| No. 2 | ... | ... | ... | 1 drachm |
| No. 3 | ... | ... | ... | 1 „ |
| Water | ... | ... | ... | 2 ounces |

And after the image begins to gain strength, the plate is

lifted out of the solution, and the development allowed to proceed with the solution imbibed by the gelatine film. By this plan all the detail can be got out without the high lights becoming choked up. When all details are out, the developer is once more applied, and proper density obtained. For instantaneous work, or where the exposure is known not to be full, we commence by soaking the plate in—

| | | | | | |
|--------|-----|-----|-----|-----|----------|
| No. 3* | ... | ... | ... | ... | 1 drachm |
| Water | ... | ... | ... | ... | 2 ounces |

After a minute's immersion in this, 3 grains of pyrogallie acid and 1 drachm of No. 2 are added, and the development proceeded with. In this case also it is often advisable to lift the plate out of the dish till all possible detail has appeared, when density can be given as before.

In developing small plates, white porcelain dishes are capital to work with, since any slight want of flatness of bottom does not cause much waste of solution; but with large plates (say, 12 by 10) these dishes are inadvisable: first, on account of their weight; and second, on account of the usual want of flatness of the bottom. For large plates shallow ebonite dishes have been manufactured, and these are everything one can wish for, if kept out of the sun, and away from heat, when they are apt to flatten out. Care should be taken to keep such dishes clean; an occasional swill with nitric acid and water helps matters much in this respect. It should be remembered that a dirty dish means a muddy developing solution.

Carbonate of Soda Developer.—The use of alkaline carbonates is gaining attention, and they certainly possess some advantages over the ammonia developer, in that they do not give rise to green fog, and that their action is slower than ammonia. Most use these developers without any restraining bromide; but we confess to liking

* Some plates will stand 2 drachms.

a slight dose of it. The formula we prefer is a very simple one, and stands as follows :

- 1.—Pyrogallic acid 3 grains
- 2.—Saturated solution of dry mono-carbonate of soda or potash... 1 drachm
- 3.—Potassium bromide solution
(10 grains to the ounce) ... 1 to 20 minims
- 4.—Water 2 ounces

It may be objected that the strength of a saturated solution of the alkaline carbonates varies according to the temperature, and this is no doubt true, but not sufficiently to be of any importance. Some use sulphite of soda with the above, No. 2, and there is no objection to this course. About ten grains of it to the ounce of saturated carbonates is sufficient to ensure immunity from yellow stains. It is the yellow stain which is the greatest objection to these developers, though, if the carbonates are pure, there is less liability to it; and even if there be a stain, a 10-grain to the ounce of water solution of citric acid after washing the plate should entirely eliminate it. There is one advantage in the use of carbonate developers, viz., that the tendency to frilling of the film is much diminished (see page 66). We have developed plates which inevitably frilled with ammonia, without a wrinkle when using the carbonates. Further on will be found a formula for developing plates with *hydrokinone* and ammonia. We may say that by using $1\frac{1}{2}$ grains of hydrokinone instead of the 3 grains of pyrogallic acid in the above formula, there is a perfect immunity from yellow or any other stain, and the negative presents the appearance of a beautiful grey black. The cost of hydrokinone is rather more than twice that of pyrogallic acid, but as only half the amount is employed there is no extra cost incurred in using it. The method of developing over-exposed, rightly-exposed, and slightly under-exposed negatives

with these developers will be readily guessed by reading the plan we adopt with the ammonia developer. . For a fully exposed picture we begin with half the alkaline carbonate given above, and if necessary add a few more drops of potassium bromide to restrain the action. For instantaneous work we soak the plate in the solution of carbonate and water, and subsequently add the pyrogalllic acid or hydroquinone without any bromide.

What is Correct Density.—It is often asked as to the length development should go. This is a somewhat difficult point to answer, as it is really dependent on the thickness of the coating given to the plate, and to the fineness of division of the particles of the emulsion. A plate that is properly coated should give sufficient density when the image appears at the back of the plate. With some kinds of emulsion the development appears to take place all through the film at once, and in this case the plate may look almost black from reduced silver before the density is complete. It must be also recollected that some plates, though apparently very dense after development, yet when they are fixed out give thinnish images. In cases of this description the development should be pushed on as far as possible. With a very thinly-coated plate, this pushing of the image to the back of the plate would give a hard negative.

The glycerine developer of Mr. Edwards, which some photographers still like, is described by him as follows:—

Make two stock solutions, and label them No. 1 and No. 2.

No. 1.

| | | | |
|------------------------|-----|-----|----------|
| Pyrogalllic acid ... | ... | ... | 1 ounce |
| Glycerine ... | ... | ... | 1 " |
| Methylated alcohol ... | ... | ... | 6 ounces |

Mix the glycerine and spirit, and add to the pyrogalllic acid.

No. 2.

| | | | | |
|--|-----|-----|-----|-----------|
| Bromide of potassium (or ammonium) ... | ... | ... | ... | 60 grains |
| Liquor ammonia, .880 ... | ... | ... | ... | 1 ounce |
| Glycerine ... | ... | ... | ... | 1 " |
| Water ... | ... | ... | ... | 6 ounces |

The above stock solutions will keep any length of time.

To make the developer, add 1 part of No. 1 to 15 parts of water, and label this bottle D (developer). In another bottle mix 1 ounce of No. 2 with 15 ounces of water, and label it A (accelerator).

It will be found convenient, to avoid mistakes, to have these two bottles of different shapes. Either of the above solutions will keep two or three days. When required for use, pour into a clean glass measure equal parts of D and A, adding the A last just before using. Place the dry, exposed plate face up in a shallow dish or tray, and pour the mixture steadily over the plate, avoiding air-bubbles. Should any adhere to the surface of the plate, at once remove them with the finger, or a camel's-hair brush kept for the purpose. Rock the dish gently, taking care to keep the plate well covered with the solution. In a few seconds the image will appear, and, if the exposure has been well timed, all the detail will be out and the development complete in about one minute, when the negative should be well washed under the tap, and placed at once in the fixing bath.

Do not hurry the development, but allow the plate to remain in the solution after all the details are visible until the required density is obtained. With this developer, used in the above proportions, there is no danger of fog, except from the action of light.

If, on the application of the mixed developer, the image flashes out and the details in the shadows appear too quickly, it will indicate that the plate has been over-

exposed; therefore at once throw off the mixed developer, and, without stopping to wash the plate, flood it with D alone, when the development will be checked, and will proceed more slowly, while the image gains in density; if too slowly, or the negative appears to be getting too intense, add a very little of A. There will, however, usually be sufficient of the latter left on the plate to complete the development with the simple addition of a sufficient quantity of solution D. A very little experience will enable the operator to produce a good printing negative from a plate which, if developed with the full proportion of A, would have been utterly useless from over-exposure. In very warm, bright weather, it will, perhaps, be found an advantage to use rather more D than A in the mixed developer, giving just sufficient exposure to avoid hardness in the negative. Under-exposure can be corrected to a certain extent by increasing the proportions of A in the mixed developer, but the addition should be made at once before the development has proceeded too far, or the effect will be to increase the density, and cause too much contrast in the negative.

These concentrated stock solutions will be found very convenient to use, and a great saving of time in weighing and measuring small quantities.

We have used the terms over-exposure, under-exposure, and proper exposure in the foregoing in this sense. A plate should develop with a developer of normal strength (such as we have given above) with the full amount of ammonia and bromide added, and the margins of the plates, which are not exposed, but covered by the rabbets of the slides, should then be free from fog, except from any small amount which may be due to halation from the sky, or other light parts of the picture. When a plate is under-exposed, the developer is insufficiently strong, and a greater strength has to be resorted to, giving a danger of general fog. An over-exposed plate means one in which there would be fog if the plate were developed

with the developer used full strength (except on the margins of the plates).

The great enemies of this developer are the air-bells which form on the plate, and they are to be feared in all developers which contain glycerine or sugar.

To develop plates made with a large proportion of gelatine, we give Mr. Bennett's directions for development with his long emulsifying process.

He soaks the plate for a minute in water in the developing dish, and then pours the following quickly along that side of the tray which is not occupied by the plate. By rocking the dish suddenly it sweeps over the plate (it is developed in five to twenty seconds):—

| | | | | |
|-----------------|-----|-----|---------|---------|
| Pyrogallic acid | ... | ... | ... | 1 grain |
| Bromide | ... | ... | ... | none* |
| Ammonia (.880) | ... | ... | 1 to 10 | drops† |
| Water | ... | ... | ... | 1 ounce |

He says:—"Do not flood with pyrogallic acid first, or you will render the plate slower; nor add more pyrogallic, or you will again slow the plate, and, moreover, have it too dense. If the exposure has been sufficiently short, you should have a dense negative, with bare glass for shadows, almost as soon as the developer has covered it. If much ammonia be used, and the plate be not developed in half a minute, fresh developer should be made, and the plate be washed."

Mr. Henderson introduced the use of ferrocyanide of potassium with the ammonia, and we give a formula. Some find it has a tendency to produce fog, whilst others have not found this difficulty. We do not much care for it ourselves:—

* For reasons for this omission, see beginning of this chapter.

† The quantity of ammonia depends on the shortness of exposure and the sensitiveness of the plate. About 4 drops may be considered as the average amount required.

| | | | |
|---------------------------------|-----|-----|-----------|
| A nearly sat. sol. of potassium | | | |
| ferro-cyanide | ... | ... | 10 ounces |
| Ammonia | ... | ... | 10 drops |
| Pyrogallic acid | ... | ... | 15 grains |

He states that if this developer be kept from light and air, it retains its developing properties a long time. If it refuses to develop, a few drops of ammonia will set its developing power in action. If free ammonia be present, and it still refuses to develop, then a little pyrogallic acid must be added.

Nelson's developer is made as follows:—

No. 1.

| | | | |
|-------------------|-----|-----|----------|
| Pyrogallic acid | ... | ... | 1 ounce |
| Methylated spirit | ... | ... | 7 ounces |
| White sugar | ... | ... | 1 ounce |
| Distilled water | ... | ... | 3 ounces |

No. 2.

| | | | |
|------------------|-----|-----|---------------------|
| Ammonia .880 | ... | ... | 4 ounces |
| Ammonium bromide | ... | ... | 1 ounce |
| White sugar | ... | ... | $\frac{1}{2}$ ounce |
| Water | ... | ... | 2 ounces |

Use 40 minims of No. 1, and from 30 to 40 minims of No. 2, mixed in 2 ounces of water.

Messrs. Wratten and Wainwright, with their ordinary or slower plates, recommend the following:—

I.—Pyrogallic acid 2 grains
 Water 1 ounce
 used freshly mixed.

II.—Potassium bromide 15 grains
 Water 1 ounce

III.—Ammonia (.880) 1 drachm
 Water 1 ounce

The plate is softened for one minute in water, 1 ounce of No. I. is applied for one minute, and then 3 minims of II. and III. are dropped into the developing cup, and the pyrogallic solution poured back. This is again poured

on, and the image develops. When development flags, 3 minims more of No. II. and III. are again added till sufficient density is obtained.

For these rapid plates (and, indeed, for most rapid plates to be found in the market), and also for plates prepared as in Chapter XXVII., use the following:—

| | | | |
|---------------------|-----|-----|-----------|
| I.—Ammonium (.880) | ... | ... | 1 ounce |
| Potassium bromide | ... | ... | 60 grains |
| Water | ... | ... | 3 ounces |
| II.—Pyrogallie acid | ... | ... | 3 grains |
| Water | ... | ... | 2 ounces |

The plate is soaked in water for a minute, when the water is poured off, and No. 2 is substituted. From 15 to 20 drops of No. I. are poured into the cup, No. I. returned into it, and applied again. The plate develops rapidly. For our own part, we like to add No. I. at two intervals of time, as the development is more under control.

All the above formulæ are given in the simplest possible form, no additions being made. Many photographers, however, add nitric acid or citric acid to the pyrogallie acid to keep it from discolouring. When using them, however, it must be remembered that a certain amount of ammonia is thereby neutralized. If nitric acid be used, 4 minims will be sufficient to keep 60 grains of pyrogallie acid free from colour.

If citric acid, about 10 grains should be used; Mr. Berkeley for the same purpose uses about 880 grains of neutral sodium sulphite to each ounce of water employed. Of all additions, we may say we prefer this last, since it has no neutralizing effect on the ammonia.

The following is a formula in which carbonate of soda is used with sulphite of soda:—

| | | |
|--|---------------|------|
| Saturated solution of washing soda | ... | A. |
| Saturated solution of sulphite of soda | ... | B. |
| Bromide of potassium | ... 20 grains | } C. |
| Water | ... 1 ounce | |

For development, take—

| | |
|-----------------|---|
| 16 drachms of | A |
| 6 drachms of | B |
| 3 or 4 drops of | C |

And add dry pyro 2 grs. to the oz. of solution.

If the pyro is preferred in solution, mix as follows:—

36 ozs. saturated solution of sulphite.

1 drop to each oz. commercial sulphuric acid.

2 drms. of pyro.

And keep in a well-stoppered bottle. Use in same proportion as given above.

In either of the formulæ given, which include carbonate of soda, carbonate of potash may be substituted. Carbonate of potash does not stain the film so much as commercial carbonate of soda.

The hydrokinone developer for bromide plates is made as follows:—

| | | | | |
|----------------|-----|-----|-----|-----------|
| 1.—Hydrokinone | ... | ... | ... | 10 grains |
| Water | ... | ... | ... | 10 ounces |

2.—Carbonate of potash, a saturated solution in water.

To each ounce of No. 1, one drachm of No. 2 is added, and about 10 drops of a (10 grains to the ounce of water) solution of chloride of sodium.

For removing the yellow colour so often seen in alkaline developed gelatine negatives, also for the use of the alum bath to avoid frilling, see the chapter on "Defects in Gelatine Negatives."

The fixing bath used will be found at page 154.

CHAPTER XXIII.

DEVELOPMENT OF GELATINE PLATES WITH FERROUS OXALATE.

DEVELOPMENT with ferrous oxalate is unquestionably the favourite method with the writer, though his partiality for it is not shared by a great many photographers. For purity of image and general excellence of quality, he believes that no developer can be compared with it. There can be no doubt that it is rather more expensive than the alkaline pyrogallate developer; but not very much so, since several plates may be developed with the same quantity of developer. It must not, however, be forgotten that after each plate is developed, a considerable amount of soluble bromide finds its way into the solution, owing to the combination of the bromine liberated from the reduced bromide combining with the potassium oxalate (see page 20). After many plates have been developed, the solution, however, is not beyond use, since a few drops of a weak solution of sodium hyposulphite are most effectual in giving it fresh developing power, and placing in sunlight, with a few grains of tartaric acid, seems to reduce the ferric salt to the ferrous state. The following are different methods of preparing the solutions.

Simple form of Ferrous-Oxalate Developer.—A saturated solution of the neutral potassium oxalate is first prepared. A crystal of oxalic acid is next added, to prevent the slightest trace of alkalinity. At one time we used to

add ferrous-oxalate to a boiling potassium oxalate solution, only so much of the oxalate being added as to leave a slight portion of the ferrous compound undissolved. We prefer now to add the ferrous oxalate to the cold saturated solution of the potassium salt, and to allow them to remain in contact with one another for twenty-four hours, shaking occasionally. The clear solution can be decanted off. This method prevents the deposition of crystals on the sides of the bottles, which always is the case if the ferrous oxalate be heated with the potassium oxalate. The solution will be of a deep red colour.

The ferrous oxalate solution rapidly oxidizes by contact with the air, as already hinted at, and our own practice is to fill 4-ounce bottles with it, cork them up, and then to lute the corks with solid paraffin. Mr. Warnerke has a still better plan. He uses a stoppered bottle having an opening near the bottom, such as can be procured at any chemical dealer's. Into this opening he fits a cork carrying a small glass tube; on to the end of this (outside the bottle, of course) he fits a piece of india-rubber tubing, and connects this with a similar piece of bent glass tubing, which reaches nearly as high as the top of the bottle. He fills the bottle two-thirds way up with the ferrous oxalate solution, and then pours in a layer of liquid paraffin oil. This prevents any access of air to the solution. To get at the solution, the bent tube is turned down below the level of the paraffin, and the developing cup or bottle filled.

Dr. Eder's Ferrous Oxalate.—Mr. York, working on the directions of Dr. Eder, gives the following formula:—

No. 1.

| | | | |
|------------------|-----|-----|------------|
| Ferrous sulphate | ... | ... | 160 grains |
| Water ... | ... | ... | 1 ounce |

No. 2.

| | | | |
|-----------------------------|-----|-----|----------|
| Potassium oxalate (neutral) | ... | ... | 1 ounce |
| Water ... | ... | ... | 3 ounces |

This makes up 4 ounces of developer, and by using these quantities, saturated solutions are obtained. Personally, we prefer 4 parts of No. 2 to 1 of No. 1.

Strong Ferrous Oxalate Developer prepared with Ferrous Sulphate.—A still stronger form of ferrous oxalate developer can be made by taking a saturated solution of potassium oxalate, and adding to it crystals of ferrous sulphate. These must be added cautiously, since part of the potassium oxalate is converted into ferrous oxalate, and the remainder holds it in solution.

Mr. York's formula for the potassium oxalate may be taken, and to it 200 grains of sulphate of iron be added (powdered up in a mortar by preference). It will probably be found that some of the yellow oxalate will precipitate, in which case *crystals* of potassium oxalate must be added to the solution till such precipitate is redissolved.

Practical Instructions for Developing with Ferrous Oxalate.—We will now suppose that we have a plate to develop by ferrous oxalate, and trace the manipulation from the beginning.

The plate is taken out of the slide in the properly-lighted dark-room, and placed in a flat dish a little larger in bottom area than itself. If the plate has a glossy surface, and has been prepared with hard gelatine, we recommend that it be soaked for five minutes in ordinary water, in order to cause the gelatine to expand vertically, and thus to soften the film. If the surface be matt, we recommend that the plate be not wetted.

Two developing solutions are prepared. Enough ferrous oxalate (by preference that prepared by the second method) is diluted with half its bulk of water, when the slight precipitation of the yellow ferrous oxalate may take place. Sufficient of the dilute solution to well cover the plate is poured over its surface, and watched for half a minute. If the image appears to be developing fairly well, and detail coming out, this deve-

loper is continued till all detail appears, when it is poured back into a developing cup, and density obtained with fresh undiluted solution of ferrous oxalate, to which 20 drops to each ounce of a 20-grain solution of potassium bromide are added. This gives density. The development should be continued till the image appears well on the surface of the gelatine next the glass plate, supposing the film to be of medium thickness. Many people recommend the dish not to be rocked to and fro; but we think it better to give a gentle motion to the liquid, as we have found that sometimes fog and stains like marble are induced by not so doing. The plate is next rinsed under the tap, and placed in the alum bath, made as follows:—Potash-alum, a saturated solution in water. It must not be supposed that this bath merely prevents frilling. It does more: it decomposes any calcium oxalate which may be formed by the water (containing lime) with which the developer is washed off. After a couple of minutes' immersion in this bath, it is placed in the fixing bath, and when all the silver bromide and iodide have been dissolved, it is washed under the tap, and the operations given at page 155 repeated.

Instead of the image coming out properly with the developer as indicated above, we will suppose that after a half a minute the high lights only slightly appear. In this case, to each ounce of concentrated developer 20 drops of a solution of sodium hyposulphite made as follows are dropped into a cup, and the dilute developer poured on to the hyposulphite:—

| | | | |
|---------------------|-----|-----|----------|
| Sodium hyposulphite | ... | ... | 2 grains |
| Water | ... | ... | 1 ounce |

The mixture is once more poured on to the plate, and if not much under-exposed for the normal developer, the details should appear rapidly and with good gradation. When all detail is out, the plate is washed, and the strong ferrous oxalate solution, with the bromide, is applied as before, to secure density.

Supposing the plate to be over-exposed, when the first developing solution is applied, the details will begin to appear too rapidly. It should be immediately poured off, and the plate flooded with a solution of potassium bromide (5 grains to the ounce of water), which should be allowed to soak into the film for a couple of minutes. It is then drained off. To each ounce of the weak solution 20 drops of the same solution may be added, and the developer applied again. This should allow the image to come up properly without flatness, but it may be desirable to finish with the strong solution as before.

Some photographers like to use old ferrous oxalate solutions, to which sodium hyposulphite is added at the commencement. This no doubt gives brilliant pictures, but is apt to cause exposure to be prolonged. On the whole, we recommend tolerably fresh ferrous oxalate if the greatest benefit is to be obtained from the developer. The developers made by mixed solutions of ferrous sulphate and potassium oxalate are not so strong as those prepared by the first method, and an allowance should be made for the difference. The latter is the more energetic developer of the two, and for instantaneous views it is recommended. Either developer, however, can be used with the sodium hyposulphite, and the difference between their detail-giving powers is then very small.

There are some plates which are unsuited for ferrous oxalate development. They are generally those which are prepared in hot weather with soft gelatine. The film shows reticulation, and the image appears granular. In that case resort should be had to alkaline development, by which this evil will be lessened. A plate worth using, however, should always stand development with ferrous oxalate.

CHAPTER XXIV.

FIXING, INTENSIFYING AND VARNISHING GELATINE NEGATIVES.

Fixing the Negatives.—A fair fixing bath is as follows :—

| | | | |
|----------------------|-----|-----|-----------|
| Hyposulphite of soda | ... | ... | 1 ounce |
| Water | ... | ... | 10 ounces |

A weaker solution, however, may be used with some plates. This reduces the chance of frilling. The use of potassium cyanide was said to be inadmissable, as it attacked the image. With some plates the following is successful :—

| | | | |
|-------------------|-----|-----|-----------|
| Potassium cyanide | ... | ... | 50 grains |
| Water | ... | ... | 10 ounces |

Before fixing the negative, it is advisable, in order to avoid all danger of frilling, as we have said in the previous chapter, to immerse it in an alum bath, which consists of a saturated solution of crystallized potash alum. The negative should be rinsed both before and after immersion. Two to five minutes in such a bath should be sufficient. The plate is next rinsed, and placed in the fixing bath. A flat dish may be used ; or, what we prefer, is a dipping bath such as used for the old wet process, as there is no evaporation, to speak of, when it is used, and the hyposulphite solution may be used until its fixing power is exhausted. And here it is that the use of iodide

in the emulsion is disadvantageous. The hyposulphite attacks iodide much less rapidly than it does bromide; hence a plate prepared with iodide takes longer to fix.

After fixing the negative it has to be thoroughly washed (unless it has to be intensified by Edwards' intensifier, see page 158). There are various contrivances for effecting this. A trough with vertical grooves to fit the plate is sometimes employed, the water entering in at the top, and being withdrawn by a small tap from the bottom. This is a good plan where many negatives have to be washed, since the heavier saline solution sinks to the bottom of the water with which the trough is filled. Where only a few negatives are to be washed, flat dishes answer, about four changes of water being given, each change being made at the end of every half hour. To ensure thorough elimination of the hyposulphite, the plate may be subsequently immersed in the alum bath, and again washed. It must be recollected that thorough washing of any film depends on its thickness, and we may say that, as a rule, we consider six hours not too long washing for a thick film. When the plate is considered washed, and is not to be intensified, it may be placed in a rack and allowed to dry spontaneously. If rapid drying be required, it may be flooded three times with methylated spirit, when it will dry very readily, and can even be accelerated by a gentle heat.

Silver Intensification.—When the intensification of a gelatine negative by any plan other than with silver is employed, the stability of the image is somewhat uncertain; though, as we shall point out, there are methods which seem to give it; but so far the test of time is wanting in them. We shall commence with silver intensification, which is uncertain in many cases, owing to the tendency of the silver to combine with the gelatine, and thus to stain the film. Now, as a rule, a gelatine negative has to be intensified *after* fixing, since the opacity of the film is usually so great that the operator

is unaware what density his negative has taken under development. It may be laid down as an axiom that, to be successful, the whole of the hyposulphites of soda and silver must be eliminated from the film, and where the film is of any thickness, this is by no means rapidly effected by simple washing. After the plate has been thoroughly washed, the gelatine film may be made more secure by applying to it a solution of *peroxide of hydrogen* in water. A drachm of what is called a "20-volume solution" to 5 ounces of water is sufficient. When it has soaked in this for half an hour, it is again washed, and intensification can commence. Another plan is, after thorough washing, to immerse the plate in fresh alum solution for half an hour, again washing thoroughly, and allow to dry, and then the intensifying may be proceeded with. Those who may have endeavoured to intensify with pyrogallie acid and silver a negative treated in the ordinary way, will find that red stains occur almost invariably where the film is thickest—that is, where the hyposulphites have not been thoroughly eliminated; and to eliminate them this extra precaution above indicated is necessary. The following intensifying solution is recommended:—

| | | | |
|------------------|-----|-----|----------|
| Ferrous sulphate | ... | ... | 5 grains |
| Citric acid | ... | ... | 10 " |
| Water | ... | ... | 1 ounce |

To this, one or two drops of a 20-grain solution of silver nitrate are added per ounce of solution, and the plate intensified as if it were a wet plate; that is, the solution is kept in motion over the surface till sufficient density is attained. Now, it by no means follows that a film thus intensified would be free from a liability to change in the presence of light, since the silver might partially combine with the gelatine. After density has been attained, the plate is washed, and put in a dish containing common salt, and once more passed into the fixing bath for a few seconds, again washed, and then dried.

The following intensifying solution may also be used :—

| | | | | |
|-----------------|-----|-----|-----|---------|
| Pyrogallie acid | ... | ... | ... | 1 grain |
| Citric acid | ... | ... | ... | 1 „ |
| Water | ... | ... | ... | 1 ounce |

Sufficient of this is taken to cover the plate, and to it is added 2 or 3 drops per ounce of solution of a solution (20 grains to 1 ounce of water) of silver nitrate. We may remark that some people flood the gelatine films, before applying either of the above intensifying solutions, with a pale sherry-coloured solution of iodine, which is dissolved in a solution of 20 grains of iodide of potassium in 1 ounce of water. There can be no harm in this, and there may be good.

Success in intensifying by either of these methods the writer has found to be more certain when the ferrous oxalate developer has been used in lieu of the ordinary alkaline developer.

We have heard of failures with these methods, and when traced to their source have almost invariably found that they arise from intensifying negatives which have been exposed to the air. It is no uncommon thing to see on such an iridescent film, to which, if silver be applied, staining is certain. In this case a very dilute solution (5 grains to the ounce of water) of potassium cyanide should be applied, and, after well washing, the intensification may begin; cyanide will generally remove any red stain which may occur if the above hyposulphite destroying solutions have been applied first.

Mercury Intensifiers.—The next intensifiers are the mercury intensifiers, some of which are most uncertain in their action, and in the permanency of the acquired density. The negative can be intensified either immediately after the washing which follows the fixing, or it can be employed upon a negative which has been dried. In the latter case the negative must be steeped for a minute

or two in water. Mr. England recommends the following as giving him what he desires :—

| | | | | |
|---|-----|-----|-----|-----------|
| Mercuric chloride (bichloride of mercury) | ... | ... | ... | 20 grains |
| Ammonium chloride | ... | ... | ... | 20 " |
| Water | ... | ... | ... | 1 ounce |

After the negative has been thoroughly washed, the above solution is poured over it till the surface assumes a grey tint. After a thorough wash (see page 154) a weak solution of ammonia (10 drops to 1 ounce of water) is applied till a dark tone is assumed by a reflected light, and brown by transmitted light. With collodion the intensity thus given is unstable, and the film has a tendency to bleach; but with gelatine negatives it is said to be permanent, though we do not vouch for it.

The next intensifier is one in which we have the greatest faith, as it gives a negative a beautiful black colour. Two solutions are made as follows :—

| | | | | |
|--|-----|-----|-----|------------|
| No. 1.—Mercuric chloride (bichloride of mercury) | ... | ... | ... | 100 grains |
| Bromide of potassium | ... | ... | ... | 100 " |
| Water | ... | ... | ... | 10 ounces |
| No. 2.—Nitrate of silver... | ... | ... | ... | 100 grains |
| Water | ... | ... | ... | 10 ounces |

To No. 2 is added cyanide of potassium, but not sufficient to dissolve the last trace of the precipitate which is formed on the first addition of the cyanide. It is convenient to make up a 100-grain solution of cyanide of potassium (which, be it remembered, is a deadly poison, and should be handled with caution) to 1 ounce of water, and to add this to the silver nitrate solution till the desired end is attained. The plate, after being dried, is soaked in water for a couple of minutes, and then immersed in a dish containing No. 1. After a few minutes the image will be found thoroughly bleached, when it is taken out and

washed for a quarter of an hour. It is then placed in a dish of No. 2 till the bleaching at the back of the plate gives place to a blackening, when it is taken out and washed thoroughly. It does not do to leave the plate too long in No. 2, as it is apt to reduce the intensity after a certain point is reached. Should the negative be now too dense, the density may be gradually and evenly reduced by immersing it in a weak solution (20 grains to the ounce of water) of hyposulphite of soda. This will take away all the acquired density if the immersion is prolonged. The negative, after this method of intensification, looks denser when wet than when dry; allowance must be made for this.

To Mr. B. J. Edwards, we believe, is due the credit of adding sodium hyposulphite to the mercury intensifier. This formula is as follows:—

No. 1.

| | | | | |
|---|-----|-----|-----|-----------|
| Mercuric chloride (bichloride of mercury) | ... | ... | ... | 60 grains |
| Water | ... | ... | ... | 6 ounces |

No. 2.

| | | | |
|------------------|-----|-----|-----------|
| Potassium iodide | ... | ... | 90 grains |
| Water | ... | ... | 2 ounces |

No. 3.

| | | | |
|---------------------|-----|-----|------------|
| Sodium hyposulphite | ... | ... | 120 grains |
| Water | ... | ... | 2 ounces |

The iodide solution is poured into the mercury solution, and then the solution of hyposulphite, which dissolves the iodide of mercury which has been formed.

The negative is fixed and washed, and the plate immersed in the above solution. Mr. Edwards says of it:—“The intensifier acts very quickly, a few seconds being sufficient to give printing density to the thinnest negative. If required to work slower, add more hyposulphite, which will also alter and improve the colour of the negative.

The shadows remain quite clear, there is no loss of detail, and the colour of the negative is all that can be desired. The negative must finally be well washed."

This intensifier we, however, do not like, as the negatives turn yellow after a time.

The Platinotype Company supply an intensifier, which is also a mercury one, but it is in combination with a platinum salt. We have tried it, and it is excellent, and apparently gives permanent intensity. The solution supplied is diluted to half its bulk, and the negative, after thorough washing, immersed in it. A chocolate colour is assumed by transmitted light, and a jet black by reflected light. The density-giving qualities of this intensifier are very great.

Uranium Intensifier.—Dr. Eder, in his "Modern Dry Plates," has recommended an uranium intensifier, which is made as follows:—

| | | | |
|---------------------------|-----|-----|-----------|
| Uranium nitrate... | ... | ... | 15 grains |
| Potassium ferricyanide... | ... | ... | 15 " |
| Water | ... | ... | 4 ounces |

Before using this, the plate must be thoroughly washed (see page 155), as traces of hyposulphite cause a reduction of the uranic salt, and a consequent slight chocolate-coloured veil over the shadows. The plate is immersed in the solution; the details in the shadows are first attacked, and then the half-tones, and finally the high-lights. This intensification is permanent, and can be used with much advantage. We prefer this one on account of its simplicity and permanency. Dr. Eder says that if a negative will not acquire sufficient intensity with uranium, it may be laid aside as useless, and with this we agree.

Varnished negatives may be intensified by removing the varnish first in warm methylated spirit, and, after rinsing under the tap, a tuft of cotton-wool should be applied to the surface. We think that there is but little more to be said regarding intensifying a negative. If

it be weak and full of detail, we much prefer to make a thin transparency in the camera, and from this another negative by contact. By this means intensity can be given to the reproduced negative, which it is almost impossible to give to the original, so that all the rapidity of the gelatine plates is secured, together with the advantage of the collodion film for intensifying. We can strongly recommend this plan to our readers, as it has been most successful in our hands.

Varnishing the Negative.—In order to prevent staining of the film by contact with silver paper during printing, a coating of varnish should be applied to the negative; but in order to avoid any chance of marking of the film, and before any varnish is applied, it is preferable that it should receive a coating of plain collodion. If it has received one to avoid frilling, it will be unnecessary to give it another. When collodion is used, the writer's experience tells him that almost any varnish will answer. Enamel collodion is, perhaps, the best to employ; or it may be made by dissolving 6 grains of tough pyroxylin in half-ounce of ether (·725) and half-ounce alcohol (·820). The collodion is poured in a pool at the upper end of the dried plate, and flowed first to the right-hand top corner, next to the left-hand top corner, third to the left-hand bottom corner, and finally, as much as possible is drained off in the bottle at the bottom right-hand corner, giving the plate a gentle rocking motion in order to cause all lines to coalesce. The plate is then set up and allowed to dry. For a varnish, Mr. England uses seed lac in methylated spirit (a saturated solution), and then thinned down till it is of a proper consistency. The Autotype Company prepare a special varnish for gelatine plates, as do other commercial houses. To apply the varnish, the plate should be gently warmed over a spirit-lamp or before the fire to such a heat that the back of the hand can only just bear the touch of the plate. The varnish is applied like the collodion. After draining off all excess, and rock-

ing the plate, it is warmed till all spirit has evaporated, and till the film is glossy. A lack of warmth will cause the film to dry "dead." Where many prints are not to be taken, it is believed that the film of collodion alone is a sufficient protection against the silver nitrate of the paper combining with the gelatine, and so causing a discolouration. If a negative does get discoloured through this, a very dilute solution of potassium cyanide will usually clear away any marking that may have been made. But great care must be taken to use this solvent in a dilute state, as when strong it attacks metallic silver when in such a fine state of division as that in which it is to be found in the gelatine plate.

CHAPTER XXV.

GELATINO-CHLORIDE EMULSION.

DR. EDER AND CAPTAIN PIZZIGHELLI worked out a gelatino-chloride emulsion, and a satisfactory method of developing it when made. The formula they gave is as follows :—

| | | | |
|---------------------------------|-----|-----|-----------|
| Sodium chloride | ... | ... | 7½ grains |
| Gelatine, hard and soft (mixed) | 25 | ½ | ” |
| Water | ... | ... | 3½ dr. |

This is emulsified by adding to it 15 grains of silver dissolved in 2 drachms of water. The silver may be precipitated and re-dissolved by ammonia, or it may be boiled and treated with ammonia, as given in Chapter XIII., page 97.

The method we adopt is the same as given in Chapter IX., viz., the boiling process.

| | | | |
|------------------------------|-----|-----|------------|
| I.—Sodium chloride | ... | ... | 80 grains |
| Nelson's No. 1 gelatine | ... | 30 | ” |
| Hydrochloric acid | ... | ... | 5 minims |
| Water | ... | ... | 1½ ounces |
| II.—Silver nitrate | ... | ... | 200 grains |
| Water | ... | ... | ½ ounce |
| III.—Nelson's No. 1 gelatine | ... | 30 | grains |
| Water | ... | ... | 1 ounce |

The above are made into solutions, and in the dark room.

II. and III. are mixed at a temperature of about 100° , and then I. added, as described in Chapter IX. The emulsion may be boiled for a quarter of an hour, or left unboiled. In either case, 240 grains of mediumly hard gelatine, or a similar total quantity of equal parts of hard and soft gelatine dissolved in two ounces of water, are added. After setting, the emulsion is washed, and plates coated as described in Chapter XIX.

The plates, when made from unboiled emulsion, are very transparent, and of a deep orange colour by transmitted light, whilst those made from the boiled emulsion are blue or sap-green.

Though extremely sensitive to daylight, they are much less so to gaslight; so that more artificial light may be used during development than with bromide plates. This will be found to be of great advantage, as the plates may be examined from time to time within a reasonable distance of a gas flame, and the density thus regulated to great nicety.

The exposure of the plates (made with unboiled emulsion) to diffused daylight will vary from one to five seconds, and the plates prepared with the boiled emulsion for from a quarter to two seconds, according to the density of the negative; whilst to an ordinary fish-tail gas burner or paraffin lamp at 12 inches distance the former will require from five to twenty minutes' exposure, and the latter from half-a-minute to three minutes. Mr. A. Cowan states that a very reliable method of exposing when a number of pictures are required exactly alike—or when it is necessary to work at night—is to burn one inch of magnesium ribbon at from 9 to 24 inches from the negative, according to its density.

Development is effected by the ferrous citrate or ferrous citro-oxalate developers, or by hydrokinone diluted to quarter strength, to which a few drops of a saturated solution of sodium chloride are added.

The ferrous-citro-oxalate developer, as introduced by the writer, is made as follows:—

| | | | |
|-----------------------------|-----|-----|------------|
| Potassium citrate (neutral) | ... | ... | 100 grains |
| Ferrous oxalate | ... | ... | 22 " |
| Water | ... | ... | 1 ounce |

The potassium citrate is first dissolved in a flask by heat, and, when nearly boiling, the ferrous oxalate is added, and shaken up in it, a cork being used to prevent the access of air to it. This quantity of ferrous-oxalate should just dissolve. It may be cooled by allowing cold water to flow over it, and should then have a citrony-red colour.

A weaker solution is made the same way with the following formula:—

| | | | |
|--------------------|-----|-----|-----------|
| Potassium citrate | ... | ... | 50 grains |
| Ferrous oxalate... | ... | ... | 12 " |
| Water | ... | ... | 1 ounce |

These solutions keep well when corked up in bottles. There is no deposit from keeping even when oxidized, which is shown by the solution turning an olive green colour.

The development is carried out in a dish, which is kept rocking. An unboiled emulsion gives a warmer tone than a boiled one.

The following is the method of making ferrous citrate developer according to Dr. Eder and Captain Pizzighelli's plan:—600 grains of citric acid are dissolved in $4\frac{1}{2}$ ounces of water with the aid of heat, and exactly neutralized with ammonia; 400 grains of citric acid are then added, and the bulk of the fluid made up to 9 ounces of water; 3 drachms of this solution are mixed with 1 drachm of a saturated solution of ferrous sulphate and 12 minims of a solution of sodium chloride (30 grains to the ounce of water).

Ferrous citrate may be purchased and dissolved in a

saturated solution of ammonium citrate, adding a little citric acid to give a clear picture.

Mr. A. Cowan has made a large number of experiments with chloride emulsion, and by a modification in development has been able to produce images which, by transmitted light, give any tone, from warm to black.

No. 1, for *Cold Tones*.

| | | | |
|---------------------|-----|-----|------------|
| Potassium citrate | ... | ... | 136 grains |
| Potassium oxalate | ... | ... | 44 " |
| Hot distilled water | ... | ... | 1 ounce |

No. 2, for *Warm Tones*.

| | | | |
|----------------------|-----|-----|------------|
| Citric acid | ... | ... | 120 grains |
| Ammon. carb. | ... | ... | 88 " |
| Cold distilled water | ... | ... | 1 ounce |

No. 3, for *Extra Warm Tones*.

| | | | |
|----------------------|-----|-----|------------|
| Citric acid | ... | ... | 180 grains |
| Ammon. carb. | ... | ... | 60 " |
| Cold distilled water | ... | ... | 1 ounce |

To 3 parts of each of these add 1 part of the following at the time of using:—

1. Sulphate of iron, 140 grains ; 2. Sulphuric acid, 1 drop ;
3. Distilled water, 1 ounce.

During development, keep the dish rocking ; the time required will vary from one to ten minutes, according to the developer used and the density required. No. 1 is the quickest, No. 3 the slowest developer.

A great variety of tones may be obtained by mixing the first and last developers together in different proportions, and altering the exposure to suit the developer.

The addition of from five to ten minims of a 10 per cent. solution of sodium chloride to each ounce of developer considerably modifies the colour, and allows of a much longer exposure. It is valuable when very rich, warm tones are required.

Still further differences in colours may be obtained by mixing one of the following with any of the preceding. The first three are, however, what Mr. Cowan recommends:—

No. 4.

| | | |
|------------------------|--------|-----------|
| Magnesium carbonate... | ... | 76 grains |
| Citric acid | | 120 „ |
| Water | | 1 ounce |

No. 5.

| | | |
|------------------------------|--------|------------|
| Sodium carbonate (common)... | ... | 205 grains |
| Citric acid | | 120 „ |
| Water | | 1 ounce |

To 3 parts of these 1 part of the sulphate of iron solution is added, as with Nos. 1, 2, and 3.

After development, the plates are washed, and fixed in clean hyposulphite of the usual strength (page 154).

The plates are then finally washed as usual.

The hydrokinone developer is made as follows:—

- 1.—Hydrokinone 6 grains
Water 10 ounces
- 2.—Potassium carbonate, a saturated solution in water.
- 3.—Sodium chloride 20 grains
Water 1 ounce

To every ounce of 1, half a drachm of No. 2 and 4 drops of No. 3 are added. The image should develop a beautiful black colour, without any stain. The ordinary alkaline developer may also be used with these plates, omitting three-quarters of the ammonia solution recommended. The image will be of a sepia brown colour, as a rule.

Mr. Arnold Spiller has introduced a developer which is somewhat expensive, but gives excellent results for these plates. The tones he obtains are beautiful, varying from purple to orange.

For the development of gelatino-chloride films, the following solutions are required:—

| | |
|------------------------------------|-----------|
| D.—Hydroxylamine hydrochloride ... | 15 grains |
| Alcohol | 1 ounce |
| E.—Potassium carbonate | 6 drams |
| Water | 1 ounce |
| F.—Ammonia 880 | 1 dram |
| Water | 1 ounce |

A normal exposure for use with this developer is about ten minutes, one foot from a fish-tail burner. For a sepia-brown tone take half a dram of D, 40 minims of E, and 1 ounce of water. For chocolate tones, the above mixture, to which has been added 1 minim of F. A purple image is obtained with half a dram of F and half a dram of D diluted with 1 ounce of water. To obtain the dichroic* tone, expose fivefold normal, and develop with half a dram of D, 6 minims of F to 1 ounce of water.

Plates prepared with the emulsion, if kept exposed to the air, are apt to tarnish, and then develop badly. They should be carefully wrapped in paper, and sealed up in tinfoil.

Lantern slides and transparencies may be taken in the camera or by contact with these gelatino-chloride plates.

* Mr. Spiller remarked that a dichroic image was formed when the following proportions of developer were used. When moist, the colour given was chestnut; and when dry, deep purple.

CHAPTER XXVI.

ACETO-GELATINE EMULSIONS.

DR. H. W. VOGEL experimented in the production of emulsions which should combine the rapidity of the ordinary gelatine plate with the ease of coating of a collodion emulsion. His emulsions are made as follows, according to the English specification of his patent. He rightly claims for himself the novelty of being able to mix a solution of pyroxyline with one of gelatine, and thus getting the advantages of both emulsions. Any gelatine emulsion (such as that described, for instance, in Chapter IX.) is prepared as usual, and the pellicle dried. This dried emulsion is then dissolved in one of the fatty acids (such as formic, acetic, or propionic; acetic acid, however, by preference, on account of its cheapness). To effect this it is warmed in the acid, using three to ten times as much acid as pellicle. The quantity of acid depends on the kind of gelatine originally employed. Sufficient alcohol is now added to this, till it is of proper consistency for flowing over the plate when heated to a temperature of about 90° F. When cold, the emulsion sets in a gelatinous mass. Plates may be coated with this emulsion like collodion, and any excess drained into the bottle. In very hot weather, however, it is better to lay the plates flat for a short time, since sufficient emulsion is with difficulty retained if they be thoroughly drained.

In order to give tenacity, Dr. Vogel, as before stated, mixes pyroxyline with his emulsion.

His formula is this :—

| | | | | |
|-------------|-----|-----|-----|-----------|
| Pyroxyline | ... | ... | ... | 20 grains |
| Acetic acid | ... | ... | ... | 1 ounce |
| Alcohol | ... | ... | ... | 1 „ |

This form of collodion is mixed with equal quantities of the gelatine emulsion just described. The plates formed by this collodio-gelatine emulsion can be used wet or dry. Another method Dr. Vogel describes, which is as follows. Collodion emulsion is prepared in the ordinary way, and dried; 70 grains of the pellicle are dissolved in 3 ounces of alcohol, and $1\frac{3}{4}$ ounce of acetic acid. 20 grains of gelatine are dissolved in $3\frac{1}{2}$ drachms of acetic acid, and added to it. Plates are coated in the ordinary manner by it.

A plan which we adopted before the publication of the formula was to take gelatine pellicle (say 50 grains), dissolve by aid of the heat of hot water in the smallest quantity of acetic acid, adding drop by drop till the solution is perfect. Methylated spirit was added till it flowed nicely over a trial plate, when it was filtered through cotton wool, washed, and was then ready for use. The plates must have a very adhesive substratum; Vogel's, given at page 115, is effective, whilst another is india-rubber in solution made by dissolving india-rubber paste in benzole till it has the consistency of cream. There is a tendency, however, with the latter for the film to crack, with the former none whatever.

The drawback to this process is the smell of the acetic acid, which is decidedly objectionable. Again, too, it is of necessity a more expensive process, since the solvents of the gelatine are not as common as tap water. On the other hand, the negatives obtained by it are excellent; the gelatine is apparently changed in quality, and allows the developer to permeate easily. The sensitiveness of

the emulsion is slightly diminished according to our experience, but there is a perfect immunity from spots of any description. There is one great convenience in this emulsion, which is, that it can be kept in a bottle corked, and used for coating plates as required, instead of having to coat more plates than sometimes may be convenient. Care must be taken, in coating the plates, that the emulsion does not run into ribs. The plates should be rocked as with collodion emulsion, and then there is no danger of this defect.

For developing, Dr. Vogel recommends the following as giving the best results :—

- 1.—Sodium mono-carbonate
(crystalline) ... 200 grains
Potassium bromide $1\frac{1}{2}$ to 2 „
Water ... $\frac{3}{4}$ ounce
- 2.—Pyrogallie acid ... 50 grains
Alcohol ... 1 ounce

3.—Four parts of No. 1 are mixed with one part of No. 2 for a normal exposure. The development must be modified according to circumstances.

Dr. Vogel also uses Nelson's developer (page 146), and the ferrous oxalate (page 150). In regard to this latter he uses it in a somewhat different form to that given. His formula is as follows :—

- 1.—Potassium oxalate (neutral) ... 10 ounces
Water ... 30 „
- 2.—Potassium bromide ... 12 grains
Water ... $\frac{1}{4}$ ounce
- 3.—Sodium hyposulphite ... 2 grains
Water ... 1 ounce
- 4.—Ferrous sulphate ... 1 ounce
Water ... 3 ounces

To develop, he mixed

| | | | | | |
|--------|-----|-----|-----|-----|----------|
| No. 1 | ... | ... | ... | ... | 1½ ounce |
| No. 2 | ... | ... | ... | ... | 15 drops |
| No. 3* | ... | ... | ... | ... | 15 „ |

When well mixed, he adds ½-ounce of No. 4, and again mixes and applies to plates.

M. Konarzewski also gives a formula for a collodio-gelatine emulsion:—

| | | | | |
|---------------------|-----|-----|-----|----------|
| Alcohol .805 | ... | ... | ... | 2 ounces |
| Glacial acetic acid | ... | ... | ... | 2 „ |
| Pyroxyline | ... | ... | ... | 18 „ |

To this collodion 180 grains of gelatine emulsion are added, and dissolved by aid of heating in hot water. He recommends a substratum of albumen and silicate of soda, which is also most effective for ordinary gelatine emulsion plates, and may be added to the list given at pages 113 and 114. It is made as follows:—

| | | | | |
|---------------------------------------|-----|-----|-----|----------|
| Stock albumen | ... | ... | ... | 1 part |
| Water | ... | ... | ... | 20 parts |
| Silicate of soda (saturated solution) | ... | ... | ... | 1 part |

These are mixed, and after allowing any precipitate to settle, the solution is flowed over the plate. With this, as, indeed, with all substrata, the plates are free from any tear-marking containing any nuclei of dust, if they are dried off over a Bunsen burner or a hot fire.

* If the plates be hard, he uses 30 drops of No. III. instead of 15.

CHAPTER XXVII.

GELATINO-BROMIDE AND GELATINO-CHLORIDE PAPERS.

THERE are in the market at the present time two or three gelatinized papers containing silver bromide, and it is to be presumed that these papers are prepared with gelatine emulsion. At first sight, nothing would appear simpler than to coat paper with an emulsion, but we may at once say that it is not by any means so simple as it seems. We will endeavour to give a description, however, of a plan by which it can be accomplished in a satisfactory manner. Firstly, the emulsion may be gelatino-bromide, gelatino-iodo-bromide, or gelatino-chloride, and may be prepared by any of the methods given in the previous chapters. It may be boiled or not boiled, according as great or little sensitiveness is required. For our own part, we like a paper which is only moderately sensitive, since there is no great need to take extremely rapid pictures. One thing, however, we may remark, that with all emulsions the resulting colour of a picture from a boiled emulsion has a greater tendency to black than one prepared without boiling. This remark also applies to gelatino-chloride emulsion, but with not such force.

The amount of water with which the finished emulsion is made will be found to be about correct ; but the operator

must, by an experiment with an emulsion, judge whether the gelatine he uses should be increased or diminished. A hard gelatine, for instance, may allow dilution with water. A golden principle to remember is, however, that the thicker you require your film, the less water there should be with the gelatine. If a film is wanted as thick as that for carbon printing, it can be obtained by using 100 grains of gelatine to each ounce of water, instead of about as much to 4 ounces of water. If a thick film, however, be required, we recommend that the operations we are going to describe be repeated twice—or even three times. It must also be recollected that a paper which is required for positive printing need contain less sensitive salt than if it be required for the production of negatives. In the former case, the emulsion may be mixed with double the amount of gelatine given at page 70, and be rather thin.

The paper to be coated should be thick Saxe paper, or paper of that description, with not too high a glaze on it. It should be cut up into the sized sheets required, and carefully dusted from every particle of dust. The emulsion should be heated and placed in a shallow dish somewhat larger than the sheet to be coated, and the fluid should be a quarter of an inch in depth. The dish must be kept warm by placing it on a closed shallow tin box containing water heated by a spirit lamp beneath, or some other similar means. When heated to about 130° F. (the temperature depending on the kind of gelatine employed), the paper is turned up for about a quarter of an inch at one end, and the sheet coiled up in a roll, the coil being made towards the turned-up end. The turned-up end is placed on the emulsion, and the coil gradually allowed to unroll itself till the whole surface except the turned-up end rests upon the emulsion. After resting a minute the end is seized by two hands, and a glass plate (to the front of which is fastened a wooden roller, the top on a level with the glass plate) having been made to

rest on the dish, the uncoated side of the paper is drawn on to the plate, where it remains till it is set,* when it is hung up by clips to dry in a cupboard or other place free from dust.

The paper thus prepared should present an even film, free from all "ridges" or "tear-markings," and, when developed, should present a vigorous image by transmitted light. Another plan, and one which answers very admirably in our hands, is to damp a piece of paper slightly larger than the size of sheet required, and stretch it over a glass plate, turning down the edges over the plate. This damped plate is given a thin coating of gelatine emulsion as in the ordinary way of using an emulsion, allowed to set, and then dried while still on the plate. For this plan the emulsion may be made rather thinner than usual. Another plan is to wax a plate with white wax and ether, leaving but little on. Coat the plate as usual; when *well set*, lightly squeegee a piece of damped paper on to the surface, and allow it to dry. By this means the paper carrying the film can be stripped off from the plate. To secure freedom from markings caused by the grain of the paper, the paper may previously be coated with a thin layer of gelatine by floating as above. The gelatine in this case should have three-quarters of a grain per ounce of chrome alum added to it.

Another very convenient method of preparing sheets of paper for negatives is by means of a *perfectly straight*



Fig. 22.

glass tube of the width of the paper, round the ends of which are two india-rubber rings, of the thickness of which the film is desired to be.

* It is a good precaution to take to place a muslin-covered frame over the glass holding the gelatinised paper to protect it from dust.

If thought advantageous, a rod may be passed through the tube, and bent round to join, and so to form a handle, by means of which the tube will revolve as it passes over any surface.

The paper is damped as before, and stretched on perfectly flat plate glass, the emulsion is poured gradually in front of the roller, and the emulsion takes a fine layer of a uniform thickness. For preparing paper for positives, a couple of sheets may be placed back to back, and together passed through a trough of emulsion, the two being raised vertically together, and dried together. The emulsion will not penetrate between the two sheets if properly manipulated.

Another plan, which we first saw in Mr. H. Starnes's hands, is very simple. The accompanying figure shows the section of a box. The emulsion is poured into A, and



Fig. 23.

the box, with the emulsion in it, is placed on damped paper, the end, C, being placed at the edge of the paper. The box is then tilted; the emulsion flows into B, and flows through C, which is a fine slit (made by inserting a thin card during the making of the box, and afterwards withdrawing it). The slit may be covered with two fine pieces of muslin if thought necessary, and the flow is thereby regulated, as the end of the box is drawn over the paper, leaving a track of emulsion. It will be seen that the box, which in our case is made of well-shellaced wood, could be made of metal (nickelled iron, for instance, or silver), and a heating box introduced so as to keep the emulsion at a proper temperature. When the box comes to the end of the paper, the emulsion is tilted back from B into A. This plan also answers for coating plates.

General Hints on Coating Paper.—When coating paper, regard should be had as to whether it is for use in the production of negatives, or merely for positives. In the former case, it is evident that the paper should have on its surface sufficient silver bromide, or its equivalent, to give a dense image by transmitted light, and this can be done in two ways, either by coating the paper with a film which is equal in thickness to that of an ordinary plate—as must be the case in some methods of coating we have indicated—or else by reducing the amount of gelatine in the emulsion. For a negative paper, we reduce the gelatine given at page 70, viz., 240 grains, to 120 or even 100 grains. It is not more wasteful than using the bigger bulk, as a thinner film is required, and the paper is more pliable. For positive paper, the amount of gelatine may be much larger when the film is of the same thickness. Approximately, it may be said that a positive only requires quarter of the density by transmitted light which a negative requires, hence the gelatine used for the former may be 400 or 500 grains, as against 100 for the latter, to an equal amount of bromide gelatine. When a bulk of emulsion is used (as it must be when paper is floated) a great consideration is to keep the emulsion homogeneous. If the temperatures be high, the small particles of bromide have a tendency to sink to the bottom of the vessel, and hence there is danger that a layer of gelatine may be at the top surface, which will contain but little of the sensitive salt. Hence our advice is to keep the temperature of the emulsion as low as possible during coating the paper, consistent, of course, with keeping it fluid. A thick layer of gelatine is very unmanageable on paper. The paper, when drying, is apt to cockle, and unless a small proportion of glycerine is added, the film is apt to break and tear. For this reason, we add to the emulsion, when the film is thick, about 20 drops of glycerine to each ounce of emulsion; and when the film is to be thin, a couple of drops are sufficient to ensure a certain amount of

pliability. We do not like glycerine, as a rule, but in this case there seems to be no help for it, particularly when the paper is to be used in a dry climate. It may also be said that a thin paper is ill adapted for coating, as then the difficulties of manipulation are much increased, and there is very little chance of getting uniformity of result.

In these methods of preparing the paper the desiccation takes place much more rapidly than with a gelatine plate, since there are two surfaces by which the drying effect of the air is utilized.

CHAPTER XXVIII.

EXPOSURE OF THE NEGATIVE PAPERS.

At first sight there is a difficulty in exposing paper in the camera, but there are three very ingenious contrivances in which to overcome it. The home-made negative paper is usually prepared in sheets, and not in lengths, and the following artifices may be employed to utilizing it.

Blocks of Sensitive Paper.—Blocks of sensitive paper are very readily prepared in a similar manner to that adopted for drawing blocks. To prepare a block, two sheets of flat zinc or tin are cut of very slightly less (say 1-16th inch) than the size of the plate which the camera is constructed to take. A dozen sheets of sensitive paper, and a similar number of smooth orange and black paper, are cut rather larger than the zinc on the plates. One sheet of zinc is placed against a couple of battons fastened on a board exactly at right angles to one another, and a sheet of orange paper is put on the zinc plate, butting also against the two battons. This is followed by a sheet of sensitive tissue, sensitive side out, and then by an orange and black paper, and again by a sheet of sensitive tissue, and so on, taking care to keep the sensitive side against the orange paper. When the last orange paper is in position, the second plate is placed on the top, and with a knife the block is trimmed, which, it may be

remarked, will only have to be done at one side and one end. The top plate is marked, and strips of paper are well coated with india-rubber solution, turned over each plate, and well pressed into the paper edges held between them. The india-rubber solution fastens the sheets of paper and tissue together at the edges. To use the block, the top tin and orange paper are removed by a point of a knife, and it is placed in the slide. When exposure has been given, the sensitive paper is removed in a similar manner, and then the black and orange paper, and another sheet is ready for exposure. Half a dozen blocks can be placed in three double backs; thus, in the slides, sensitized surfaces to take seventy-two pictures can be conveniently carried. We have found that the ordinary orange paper used by stationers has no noxious effects on the sensitive films.

Holders for Single Sheets.—These can be made by any one. Cardboard, a wooden board, or ebonite of exactly the same size as the paper, are used as the backing. A mask is made in brass or galvanized iron, and curled over this board; the paper is placed on the board, and the two are slid into the mask. Again, a flat zinc mask of the size of the plate, cut out within $\frac{1}{4}$ -inch of the margin, may be placed in the slide, the paper on this, and then it may be backed with a glass plate.

The Roller Slide.—Many years ago Mr. Melhuish introduced a roller slide for endless paper, and more than ten years ago Mr. Warnerke introduced one which was very admirable in its working, and of which we have a most excellent specimen which was adapted for collodion emulsions. Lately Mr. Warnerke has still further modified the slide, and made it more adapted for the gelatine. On the Continent, several have been made in the same direction. The latest, however, is the Eastman-Walker slide, which is ingenious in construction, and very effective. The following is taken from their printed description.

“The roll-holder consists essentially of a metal frame

carrying the spool wound with the supply of paper, and a reel for winding up the exposed paper, suitable devices for maintaining a tension upon the paper, and measuring and registering mechanism.

The frame is hinged at both ends to the panelled board which forms the back of the enclosing case. Fig. 24

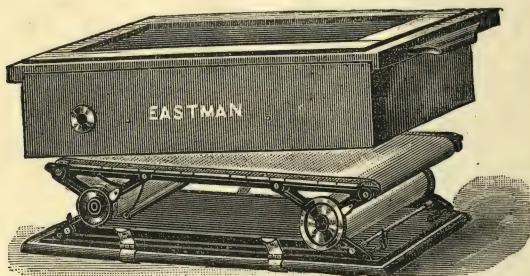


Fig. 24.

shows the holder with the case partly raised, fig. 25 the movement raised for changing the spool.

“ To fill the holder, the movement is raised as shown, the spool inserted in its place under the brake, and fastened with the thumb-screw on the side of the frame ; the pawl on the tension barrel is thrown off, the band on the spool broken, and sufficient paper drawn out to reach over the bed to the reel ; the movement is shut down and fastened and raised at the reel end ; the paper is then drawn over the guide roll and slipped under the clamp on the reel, and the reel turned sufficiently to give the clamp a hold on the paper. The pawl on the tension drum is now thrown in, the tension put on by turning the tension barrel over to the left until the paper is taut ; the movement is shut down, the case put on, the key is inserted, and turned until an alarum strikes once. The slide is drawn, and the limits of the first exposure marked with a lead pencil. The holder is then ready to attach to the camera. After the first exposure, turn the key until the alarum strikes

four times (three in the 4 by 5 holder), and this brings a fresh sheet on to the bed for exposure. When the required number of exposures have been made, take the holder into the dark room, take off the case, and insert the point of a pen-knife in the slot in the guide roll, and separate

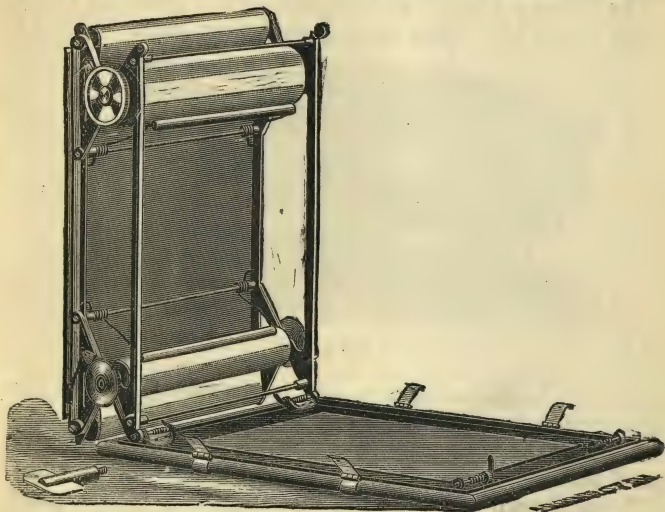


Fig. 25.

the exposed from the unexposed by drawing it along the slot. Throw off the pawl from the reel, and draw out the exposed paper, and cut it off at every fourth mark (third mark in the 4 by 5 holder) with a pair of shears. If any unexposed paper remains on the spool, draw over the end, and attach it to the reel as before, and the holder is ready for work again. The holder should be carefully dusted out before filling."

CHAPTER XXIX.

DEVELOPMENT OF GELATINO-BROMIDE PAPER FOR NEGATIVES.

To develop any of the negative papers, whose manufacture we have briefly described, the ordinary alkaline developer, to which sulphite of soda has been added, may be employed (see page 147), or the developer recommended by Mr. Warnerke, or the Eastman Dry Plate Company. The ferrous-oxalate developer is also excellent, but care must be used to avoid stains, due to oxides of iron being formed. This is best attained by the use, after development, of a saturated aqueous solution of alum, to which one per cent. of sulphuric acid has been added. In every case, before development, the paper is soaked in water, and the developer applied. Density can be judged by looking *through* the paper, but allowance must be made for the density of the paper itself. A negative should appear denser than it does on a glass plate. The development should continue till but faint glimmers of white paper are seen on the image, and therefore it will appear under-exposed when fixed. After developing, it should be passed through the alum bath, and be allowed to remain there for a quarter of an hour, when it should be *thoroughly* washed for half an hour, and then be fixed, and again washed. Several negatives may be developed at one time, if two solutions in separate dishes are at hand,

one being old restrained developer, and the other new. If the image appears too quickly in the fresh solution, it is immediately passed into the restrained solution, when the development will progress more slowly.

One advantage of this paper, on which to take negatives, is that commercially it can be made in long strips, and used in a roller slide, and in any case the weight of glass is avoided; another advantage is that the negatives may be used as reversed if required; and a final one is that the storage of these films is easy, a dozen or more going in an envelope.

Mr. Warnerke has recently introduced into the market several kinds of paper coated with gelatine emulsion, for producing negatives.

Negative Tissue.—The first paper he calls negative tissue. It consists of stout paper coated with gelatine and gelatine emulsion, and so prepared that after development, fixing, and drying, it can be peeled off from the paper, and is a flexible negative, from which prints can be taken. The following is the method of developing employed by Mr. Warnerke:—

The exposed sheet of tissue is placed in a developing dish and moistened under a tap with water (both sides), so that it will adhere to the bottom of the dish. It is then developed like an ordinary glass plate.

The following developer is especially recommended:—

| | | | | |
|------------------------|-----|-----|-----|-----------|
| A.—Pyrogallol | ... | ... | ... | 6 grains |
| Citric acid | ... | ... | ... | 1 grain |
| Sodium sulphite... | ... | ... | ... | 12 grains |
| Water | ... | ... | ... | 1 ounce |
| B.—Potassium carbonate | ... | ... | ... | 22 grains |
| Sodium sulphite... | ... | ... | ... | 6 " |
| Water | ... | ... | ... | 1 ounce |

Equal proportions of A and B are mixed together and applied to the plate. After development, the tissue is rinsed in two or three changes of water, and immersed in

a strong solution of common alum, washed, then fixed with hyposulphite of soda, and washed again thoroughly. The tissue bearing the image is next spontaneously dried. In hot and dry weather it is advisable to add a small quantity of glycerine to the last washing water to render the film more pliable. The film will be much improved if the tissue, after the last washing, is squeegeed to a glass plate prepared with talc (French chalk), and allowed to dry on it. It may happen, especially when washing has been too long, that the tissue will curl so much, that it will be difficult to attach it to the glass or to lay it flat. In this case it will be useful to press it for some time between two glass plates, putting some blotting-paper behind to remove the excess of water absorbed by the film. When the tissue is quite dry, the film is detached from the paper support, beginning by one of the corners, and slowly, but steadily, proceeding until all the film is detached.

The printing can be made from either side of the film, making this negative tissue specially useful for many processes in which reversed negatives are required. Finished film negatives are best kept between sheets of stout unsized paper. Retouching on the film can be made as on a glass plate.

Negative Paper.—Mr. Warnerke also prepares another paper which is very useful in some ways. It consists of a film of gelatine emulsion, the portions of the film which do not contain the silver reduced by development being removed.

In case an ordinary negative is required, the image is first transferred to the flexible support as in carbon printing, which is paper coated with an insoluble form of gelatine, and to which the adhesion of another layer of gelatine is incomplete; that is to say, it can be separated from it after drying. The paper negative, after it is developed, is squeegeed on to this, in the same way as on to the glass, in the following manner:—

The two pieces of paper—*i.e.*, the developed paper and the flexible support—are placed face to face with a layer of water between them, and then placed on a glass plate or other smooth surface. A squeegee—a bar of thick rubber let into a wooden holder—is then brought to bear on the back of one of them, the water squeezed out, and the two left in contact for a short time. The papers are then placed in hot water of about 100° F., the paper on which the emulsion was originally coated is stripped off, and the soluble gelatine, which is free from any image, is washed away, leaving the image on the temporary support. When moist—either being moistened after drying, or immediately after development—the surface of the paper on which the image rests is transferred to a glass plate, to which has been given a thin coating of gelatine, the squeegee being again brought into requisition to bring the image in close contact with the surface of the glass. When dry, the transfer paper peels off, and leaves the image on the plate.

If a reversed negative is required, all that is necessary is, after development, to squeegee the developed paper on to a sheet of clean glass, instead of on to the temporary paper support, and then to allow it to soak in warm water. The paper backing is stripped off, and the gelatine film left behind.

A paper which can be used for this process may be prepared by giving it a coating of india-rubber solution, or gelatine, and then a coating of normal collodion (10 grains of pyroxyline to 1 ounce of ether and 1 ounce of alcohol). The paper thus prepared may be coated by turning up the edges to form it into a little dish, and holding it on a glass plate. The emulsion is then allowed to set, and eventually hung up to dry.

The object of this process is that, no matter what developer is used, the negative should be without stain, and can be intensified by pyrogallie acid and silver (see page 157) without any chance of injury to it. The *rationale* of

the process is this : that a pyrogallic acid and also a hydrokinone developer renders the gelatine insoluble where the metallic silver is reduced, the remainder being left soluble. Now as the reduction of the silver takes place first on the surface of the gelatine film, it is quite evident that the soluble portion must be enclosed between the top surface and the paper support, and that to get rid of it, the back surface of the gelatine must be exposed, as in carbon printing.

The warm water dissolves away the soluble gelatine, and leaves the image of metallic silver and insoluble gelatine behind, the latter being exactly proportional to the amount of silver precipitated. Besides this, there is the silver bromide which has not been reduced, left behind entangled in the film, which gives greater density. This may be removed by fixing in sodium hyposulphite as usual if required. The insolubility of the gelatine seems to be greatest 1st, where the pyrogallic acid (or hydrokinone) is in excess of that usually employed ; or 2nd, where the alkali is in excess. With the ordinary strength of developer, the insolubility appears to be but partial.

The developer for this negative paper is the same as that for the negative tissue. The relative proportions of the solutions A and B is very important. The object of the developer is not only to render the image visible, but also to render it insoluble. Excess of one solution over the other can produce either total insolubility of the whole film, or the reverse, too much solubility.

Double Surface Negative Paper.—The latest negative paper which Mr. Warnerke has introduced is one which he has patented, and consists of a paper coated on both sides. It is claimed that by this means the grain of the paper is done away with—or, rather, that it does not show. The reason of this is that the gelatine emulsion with which the back surface of the paper is coated receives the light obstructed by the grain. Where the grain is thin, the light acts more vigorously than when it is thicker, and on deve-

lopment the result is that the opacity remains nearly the same in every adjacent part. This of course is more particularly true when the image is vigorous than when it is weak. The paper used in this process is chemically prepared, and made transparent to begin with, which is an important point, since the more transparent it is the quicker it will print. Any developer may be used with this tissue, either ferrous-oxalate or ordinary alkaline developer, or the alkaline carbonate developer (see page 184). After development the negative is fixed in the ordinary way after passing through the alum bath, and then washed, and, if necessary, to remove any slight stain, is passed through a bath containing two or three drops of sulphuric acid to the ounce of water, when it is again washed. The paper may be dried in contact with glass, or not; in the latter case, and in order to render it flat, it is placed between sheets of blotting-paper very slightly damped and put under pressure, and, when limp, transferred to a pressure frame, and kept there till dry. The negative prints very nearly as rapidly as if it were on glass. Care must be taken that both sides of the paper are well wetted before development, and that the bottom of the developing dish is well covered with water, otherwise the gelatine surface will stick to the bottom of the dish, and mar the negative. During development the paper should be turned over frequently to secure an evenness, and the image should appear strongly on the surface of the paper which was away from the lens.

Eastman's Negative Films.—Eastman and Co. have introduced negative paper which gives very good results. The paper is ordinary unglazed paper, and for printing requires making transparent by oiling. They recommend the following developer for it:—

| | | |
|---------------------------------------|-----|----------|
| No. 1—Sodium sulphite crystals (pure) | ... | 6 ounces |
| Distilled or boiled water | ... | 40 " |
| Pyrogalllic acid | ... | 1 ounce |

| | | | | | |
|-------------------------------|-----|-----|-----|-----|---------------------|
| No. 2—Sodium carbonate (pure) | ... | ... | ... | ... | $\frac{1}{4}$ pound |
| Water | ... | ... | ... | ... | 1 quart |

To develop, take in a suitable tray—

| | | | | | |
|-------|-----|-----|-----|-----|---------|
| No. 1 | ... | ... | ... | ... | 1 ounce |
| No. 2 | ... | ... | ... | ... | 1 „ |
| Water | ... | ... | ... | ... | 1 „ |

Immerse the exposed paper in clean *cold* water, and with a soft camel's hair brush gently remove the adhering air-bells from the surface. As soon as limp, transfer to the developer, taking care to avoid bubbles, by gently lowering the paper by one edge, so as to slide it under the surface of the developer.

The image should appear in ten to twenty seconds, and the development should be carried on in the same way as for a glass dry plate. If the image appears too quickly, and is flat and full of detail, add five to ten drops of the restrainer—

| | | | | |
|-------------------|-----|-----|-----|----------|
| Potassium bromide | ... | ... | ... | 1 ounce |
| Water | ... | ... | ... | 6 ounces |

This will keep back the shadows, and allow the high lights to attain density.

If the exposure has been too short, and the image does not appear except in the highest lights, add, instead of the restrainer, not to exceed one ounce of No. 2; this will help to bring out the details, and compensate in a measure for the short exposure. As soon as sufficient density is obtained, slightly rinse the negative, and put in the fixing bath—

| | | | | |
|---------------------|-----|-----|-----|---------------------|
| Sodium hyposulphite | ... | ... | ... | 4 ounces |
| Water | ... | ... | ... | 1 pint |
| Common alum* | ... | ... | ... | $\frac{1}{2}$ ounce |

To be mixed fresh for each batch of negatives.

* We do not recommend this.

The completion of the fixing operation may be ascertained by looking through the film. When fixed, wash in five or six changes of water for fifteen or twenty minutes, and then lay the paper negative, face down, upon a clean plate of glass or hard rubber that has been rubbed over with an oily rag. Press the negative into contact with the plate by the scraping action of a squeegee, and allow to dry, when it will peel off from the plate with a fine polished surface.

The ferrous oxalate developer also works well with Eastman's improved negative paper, and we recommend it for trial.

Oiling.—Lay the negative down on a clean sheet of paper, and give it a coat of castor oil, applied with a rag. Then press it with a hot iron until it shows an even dark colour. Use plenty of oil. If the iron is too hot it will dry out the oil, and it will be necessary to go over it with the rag again. If the iron is not hot enough, it will fail to cause the oil to penetrate the paper sufficiently. When an even colour is obtained, wipe off the excess of oil with a soft cloth, and the negative is ready to print.

Instead of using a hot iron, the negative may be held over the stove until the oil sinks into the paper. The hot oil expels the air in the paper and fills the pores, so that on examination it will be found that the grain has disappeared, leaving a fine ground glass effect. No oil should be allowed to get on the face of the negative; in case it does, it may be removed with a cloth and a few drops of alcohol.

Printing.—Thus prepared, Eastman's negative paper will print remarkably free from grain, and quicker than most pyro and ammonia developed glass negatives. To print, simply lay the negative, with the glossy side up, on a piece of glass in the printing frame, and print the same as a glass negative. The negative does not require fastening to the glass in any way. These negatives should be kept between paraffined paper, or back to back

in a printing frame, or suitable box. If the oil dries out after continued use, the negative may be re-oiled.

Retouching.—When the negative is to be retouched, as in portraiture, it should be done after oiling. The paper takes the pencil freely, and persons unskilled will find it comparatively easy to “work” these negatives. Amateurs can spot their own negatives, and work-in fine cloud effects with a stump on the paper surface.

Intensification.—When it is necessary to intensify, it may be done before oiling by soaking the negative in a saturated solution of corrosive sublimate, washing, and then blackening the image with a solution of ten drops of strong ammonia per one ounce of water.

Where strong negatives are desired, add five drops of the restrainer to the developer before using.

Waxing the Negative.—We have found that the negative may be waxed, instead of oiled, as the Eastman Company recommend, and for most paper, such as we have prepared, it is very efficient. A flat iron is heated, and whilst drawn over the back of the negative a piece of white wax is held against it. This leaves a layer of wax on the paper. There will always be an excess of wax, but this can be well removed by clean blotting-paper being placed on the waxed surface, and the flat iron, moderately heated, being drawn over the surface. Instead of this method, a cream of white wax in turpentine, made with the aid of heat, may be applied with cotton-wool or a soft rag, all excess being wiped off.

CHAPTER XXX.

DEVELOPMENT OF POSITIVE PAPER.

FOR direct enlarged positives, the thinly-coated bromide papers are extremely useful, an optical lantern can be used, and good prints secured with but short exposure. As an example of the exposure necessary, we have produced an enlargement of six diameters by an exposure of three minutes when using a triple-wick oil lamp as the source of illumination. They also should take the place of collodion transfers for working upon in oils or crayons.

Bromide Positive Paper.—To develop a bromide or bromo-iodide emulsion, we recommend a ferrous oxalate developer, using to every ounce employed about 10 drops of a 20-grain solution of potassium bromide. This gives a blacker image than the ferrous oxalate alone. One firm recommend the following developing solutions:—

Stock Solutions.

| | | | |
|---------------------------------|-----|-----|---------------------|
| 1.—Chrome alum ... | ... | ... | 100 grains |
| Boiling water ... | ... | ... | 5 ounces |
| 2.—Oxalic acid ... | ... | ... | 30 grains |
| Water ... | ... | ... | 5 ounces |
| A.—Potassium oxalate ... | ... | ... | 4 ounces |
| Glycerine ... | ... | ... | $\frac{1}{2}$ ounce |
| Chrome-alum solution (No. 1) | | | $\frac{1}{2}$ " |
| Oxalic-acid solution (No. 2)... | | | $\frac{1}{2}$ " |
| Water ... | ... | ... | 15 ounces |

| | | | |
|---------------------|-----|-----|-----------|
| B.—Ferrous sulphate | ... | ... | 4 ounces |
| Sulphuric acid | ... | ... | 10 minims |
| Water | ... | ... | 16 ounces |

To develop, 8 parts of A are mixed with 1 part of B.

An excellent developer may be made by mixing equal portions of the ordinary oxalate developer and the above. For fixing—

| | | | |
|---------------------|-----|-----|----------|
| Sodium hyposulphite | ... | ... | 4 ounces |
| Water | ... | ... | 20 „ |

They further recommend the following for bleaching if necessary :—

| | | | |
|----------------------------------|-----|-----|------------|
| A saturated solution of borax or | | | |
| sulphuric acid | ... | ... | 1 ounce |
| Water | ... | ... | 100 ounces |

And to harden the film, common alum (a saturated solution), or chrome alum of a strength 20 grains to each ounce of water.

The bromide and bromo-iodide papers may also be developed with the usual alkaline developer, using citric acid to keep the solutions from discolouring. The addition of sodium sulphite, as recommended by Mr. Berkeley, will answer the same purpose. Hydrokinone and the carbonates of potassium or sodium (see page 148) are also excellent, leaving no stain on the paper. The fixing bath should be the same as above. When the washing is complete, which will take two or three hours, the prints may be toned if required. A beautiful brown-black tone is given by a weak solution of ammonium sulphide, the colour being permanent. All excess should, of course, be well washed out. A solution of sulphuretted hydrogen in water will answer the same purpose. Against the use of such solutions we are aware that many photographers will, metaphorically, hold up their hands, as they will remember the dread they have of bringing any sulphur compounds in contact with a print on albumenized paper. They should

recollect, however, that the conditions are totally different. It is the organic compound of silver which gives rise to fading, and *not* the sulphuration of the metallic silver. Sulphide of silver is about as permanent a silver compound as can exist, and there can be no danger of its fading. Great care must be taken to eliminate all traces of iron salts by washing after development, when using the above solutions, otherwise the whites will be dirty. This dirty green appearance, however, may be got rid of by passing the print through dilute hydrochloric acid.

An improvement in the tone may also be given by using the uranium intensifier (see page 160). Resort may also be had to gold toning; but the above will give almost every variety.

Chloride Positive Paper.—Recently there have been brought into the market several brands of rapid printing paper for development. Most of them are gelatino-chloride papers; some, however, have mixtures of bromide with them. The advantage of this brand of paper is, that it may be developed and then toned to almost any desired colour.

We have prepared paper which answers every requirement by the formula given at page 163, using three times the quantity of added gelatine. It is preferable that it should be unboiled, or, at all events, only very slightly boiled, in order to get a warm tone.

The following developer is recommended:—

| | | | | | |
|--------------------------|--|--|--|--|------------|
| No. 1.—Potassium oxalate | | | | | 125 grains |
| Potassium bromide | | | | | 5 „ |
| Water | | | | | 1 ounce |
| No. 2.—Ferrous sulphate | | | | | 50 grains |
| Water | | | | | 1½ ounce |

3 parts of No. 1 are mixed with 1 part of No. 2, and 2* ounces of water.

* Some recommend 2 ounces of a 5 per cent. solution of sodium sulphite to replace these 2 ounces of water.

The longer the exposure within limits, the more warm is the tone produced; a warm tone is not produced if the exposure is short. An exposure of half a minute in diffused daylight should be sufficient to give a warm tone. The image should be developed till it appears rather darker than it should finally be. It is next well washed, and then placed in a saturated solution of alum, where it is left for a quarter of an hour. It is taken out and washed for a quarter of an hour, when it may be toned. The following toning bath (the sel d'or) is recommended:—

| | | | |
|-------------------------|-----|-----|-----------|
| A.—Hyposulphite of soda | ... | ... | 30 ounces |
| Water | ... | ... | 30 „ |
| B.—Gold chloride | ... | ... | 15 grains |
| Water | ... | ... | 20 ounces |

To solution A add, slowly and well stirring, 4 ounces of B. The bath is then ready for use. It improves by keeping, and, when necessary, is replenished by the addition of fresh hyposulphite of soda, and of gold solution B.

The print is to be kept in this bath for ten minutes, when it will be both toned and fixed.

The following acetate of soda toning bath also answers well:—

| | | | |
|--------------------|-----|-----|-----------------|
| Gold chloride | ... | ... | 1 grain |
| Acetate of soda... | ... | ... | 30 grains |
| Water | ... | ... | 8 ounces |
| Chloride of lime | ... | ... | a slight trace. |

The lime toning bath, and the borax bath,* may be used.

After the print is toned in any of the above baths (except the sel d'or), it must be fixed in a two per cent. solution of hyposulphite of soda.† It is again washed, and then dried in contact with some smooth flat sur-

* For details, see "Instruction in Photography" (Piper and Carter).

† Mr. Ashman finds, we believe, that if the prints, before toning, were immersed in a weak solution (say, half per cent.) of ammonium sulphocyanate for a short time, the toning colour was more satisfactory.

face. It was originally recommended to use a glass surface which had been rubbed over with powdered talc, but we have found that the gelatine was liable to stick to the glass. If the glass be rubbed over with castor oil, however, it may be used, and a fine surface is given to the print. Perfectly smooth ebonite or ferrotype plates may also be used. A print after washing is placed, face down, in a dish with the surface to which they are attached beneath. The two are raised out together with a layer of water between, when a squeegee is brought to bear on the former, the water squeezed out, and the two surfaces brought into close contact. They are then placed to dry, and when desiccation is perfect, the two can be detached. The mounting of these prints is somewhat difficult, on account of damp spoiling the gloss of the surface. Mr. Warnerke finds that if the prints are not burnished, sufficient surface is given to the prints, and there is no need to dry them in contact with the support.

This printing by development is still in its infancy, and before long we may expect much improvement in the preparation of the paper and also in its development. It may be remarked that prints on this paper may be taken in the camera, thus avoiding the necessity of taking enlarged negatives.

CHAPTER XXXI.

DEFECTS IN GELATINE PLATES.

Frilling.—What is meant by frilling is the gelatine film leaving the glass plate in folds or wrinkles; and a greater nuisance than this cannot be met with. It generally occurs when fixing the plate, though we have sometimes met with it during the development, especially in hot weather. We will endeavour to state the causes of frilling as far as they are known. Frilling is often caused by the use of unsuitable gelatine, possessing but little tenacity. The more the qualities of gelatine are like glue, the less chance there is of meeting with this vexatious evil. If gelatine, however, were like glue in respect to hardness, the difficulty of developing a plate would be very great, since it is too hard. The addition of chrome alum to an emulsion also prevents frilling to a great extent. The objections to chrome alum are that it increases the tenacity of the gelatine, and prevents easy development; hence it should be used sparingly.

Gelatine that has been heated for a long time has a special tendency to frill, and, unless fresh gelatine be added to the emulsion, in some cases frilling is inevitable. Long cooking (in warm weather particularly) means decomposition of the gelatine, and decomposed gelatine is very detrimental in preparing a dry plate. Boiling for a short

time has much the same effect on the gelatine as cooking at a lower temperature; hence, to avoid frilling, it is better not to boil the emulsion with the full amount of gelatine.

Another source of frilling is the plate being improperly cleaned. If water will not flow in a uniform sheet from a plate, it may be well understood that there will be but little adhesion between it and an aqueous solution of gelatine. This we believe to be one fruitful source of evil.

Another source of frilling is unequal drying. Thus, if plates be dried in an unventilated box, it will usually be found that a central patch refuses to dry till long after the outsides are completely desiccated. At the junction of this central patch with the neighbouring gelatine frilling is to be looked for. It will spread to the parts which have been the longest in drying. This is due to a false tension set up in the film, and can only be conquered by drying the plate by means of alcohol, or by using a proper drying cupboard.

Again, when plates are coated in hot weather, unless precautions are taken of cooling the slabs on which they are placed, they take long to set. The emulsion remains liquid on the plate for sufficient time to allow the heavier particles of silver bromide* to settle down on the surface of the glass. This of course diminishes the surface to which adhesion can take place. We believe that most of the frilling which takes place in plates prepared in hot weather may be traced to this cause. When washing after fixing, frilling is often caused by allowing a stream of water from the tap to impinge on the plate. This should never be allowed if the film is at all delicate. Plates which frill or blister will often not show any signs of so doing if kept for a few months.

* This is particularly liable to happen when the emulsion has been long boiled or carelessly mixed.

A general remedy for frilling is to coat the plate with normal collodion containing about six grains of tough pyroxyline to the ounce of solvents. The formula would be thus:—

| | | | |
|------------------|-----|-----|---------------------|
| Tough pyroxyline | ... | ... | 6 grains |
| Alcohol (.820) | ... | ... | $\frac{1}{2}$ ounce |
| Ether (.725) | ... | ... | $\frac{1}{2}$ " |

This may be applied to the film immediately before developing the plate: the solvents are washed away in a dish of clean water first, and, when all repellent action is gone, the developing solutions applied. If the film has been allowed to dry, a solution of one part of ether to three of alcohol will render it pervious to the developing solutions.* In some batches of plates frilling is so obstinate that, although collodion be applied, the film has a tendency to curl off from the edges of the plate. It is advisable, when such is suspected, to run a brush with an india-rubber solution round the edges, to prevent the water having access to that part of the film. When fixing such plates, it not unfrequently happens that blisters appear, and, if allowed to remain as they were, will spoil the negative. To avoid this, we wash the plate under the tap till all the blisters join, and the film presents the appearance of a sack containing water. A prick at one corner of the plate lets this liquid free, and the washing can take place as usual.

Some writers state that, by immersing the plate in a saturated solution of Epsom salts, frilling is avoided; we have not succeeded ourselves in proving its efficacy.

Blisters on the Film.—Blisters on the film are the usual preliminaries to frilling. When they commence, further damage may usually be avoided by flooding the plate with methylated spirit. This extracts the water, and with it

* We have found this essential in intensifying negatives which have been treated with collodion after fixing and drying.

any soluble salt that may be left, and the plate speedily dries, which is an advantage if it be fixed. Blisters are usually found to follow the rubbing marks of the polishing cloth, if such be used. The cure here is self-evident. They also are to be found in places between which the film has dried quickly and slowly.

Red Fog.—The writer fortunately knows very little about this disaster, but it is found to occur if the silver nitrate is in excess of the salts with which it should combine. Cyanide will sometimes eliminate it from a film, but this remedy must be used with caution.

Green Fog.—This fog is green by reflected light, and pink by transmitted light, being dichroic. Experiment points to it being reduced metallic silver in an exceedingly fine state of division, this reduction being aided by decomposed gelatine. In some cases we have immersed the film in a strong solution of bichromate of potash, and on afterwards washing, the fog has disappeared; but whether it is a certain cure, we hesitate to say; it is, at any rate, worth trying.

The writer found that green fog can be eliminated from a plate if, after fixing and washing, it is treated with a ferric salt. The following seems to answer satisfactorily:

| | | | |
|-------------------|-----|-----|-----------|
| Ferric chloride | ... | ... | 50 grains |
| Potassium bromide | ... | ... | 30 " |
| Water | ... | ... | 4 ounces |

This converts the image into silver bromide, and at the same time bleaches the green fog, which, seemingly, is a deposit of silver mixed with a constituent of gelatine. The plate is then washed to get rid of any great excess of the iron salt, when it is treated with ferric oxalate developer. This reduces the bromide, with slightly increased density, to the state of metallic silver, and the green fog is replaced by a *very faint* deposit of metallic silver, which in no way interferes with the printing. Green fog is never seen when using ferrous

oxalate, which has not an alkaline reaction on the alkaline carbonates.

General Fog.—By general fog we mean the fog produced in development, caused by the partial reduction of the silver salt all over the film. This is probably due to the decomposition of the gelatine by long cooking, the products of which in the presence of a developer are apt to react on the silver salt, and produce a partial reduction in it. The production of this kind of fog, and electrical disturbance in the atmosphere, are apt to go together. In unfavourable weather, a few drops of a solution of carbolic acid should be added to the gelatine during boiling or prolonged emulsification; this will generally check or entirely prevent the decomposition. An excess of silver is likewise very likely to produce the evil, but the presence of iodide in the emulsion will almost certainly cure it. Another fruitful source of fog is the light admitted to the plates during preparation or development. The light should be tested by putting a plate in the dark slide, and drawing up half the front, and exposing the half-plate to the light for ten minutes. If the fog be due to this cause, the plate on development is sure to show it by a slight reduction of metallic silver in the part so exposed.

Whatever may be the cause of fog—if the emulsion be not hopelessly in fault, or if the plates have seen light—we have found that, as in the collodio-bromide process, there is one certain sure cure. If the emulsion be slightly at fault, squeeze it into water containing ten grains of potassium bichromate to each ounce, and about an equal part of some soluble bromide, and allow it to rest for an hour, and then wash again for a couple of hours more. If all the bichromate be not taken out by this washing, it is not of much consequence, since, when dry, it is inactive. The sensitiveness after this treatment is not much diminished, and the negatives taken with it are beautifully bright. Plates may be treated in precisely

the same manner, and give unveiled pictures. There is a *slight* diminution of sensitiveness if the bichromate be not all washed out, but nothing to hurt except where very great rapidity is required.

A cure for any emulsion is the addition of a few grains of cupric chloride. This diminishes the sensitiveness, but is most effectual, negatives yielding bright and brilliant images. A remarkable fact about the addition of the cupric chloride is, that the grey form of bromide is converted into the red form if much of the copper salt be employed. The addition of a few grains of ferricyanide of potassium with a little bromide of potassium (according to Dr. Eder) is also a perfect cure, but this slows the emulsion.

Another method is to add two drops of a mixture of hydrochloric and nitric acids slightly warmed so as to change the colour of the emulsion, or to slightly acidify the first wash water with it; about one drachm to a pint of water is generally ample. The length of time which the emulsion should be in contact with the acidified water depends on the size of the mesh of the canvas through which the emulsion is squeezed. For a medium size, half-an-hour suffices. The emulsion has a tendency to become insoluble by this method.

Flatness of Image is usually due to over-exposure and development with the alkaline developer: the use of ferrous oxalate mitigates the evil, whilst if iodide be in the film, we have never found any great lack of density to arise. An over-exposed picture can be made to yield a dense image by slow development. Feebleness of the image is also often caused by too thin a coating of emulsion, or an emulsion poor in silver salt. A thick film is a desideratum, giving all the necessary density to the image with facility. When a vigorous image is required, it is most readily obtained by using a *freshly-prepared* and strong ferrous oxalate solution (see page 149).

Too Great Density of Image is sometimes met with, and

can be remedied by applying ferric chloride to the film, and then subsequently immersing in the hyposulphite of soda fixing bath.

The formula recommended is—

| | | | |
|--------------------|-----|-----|----------|
| Ferric chloride... | ... | ... | 1 drachm |
| Water ... | ... | ... | 4 ounces |

This is flowed over the plate a short time, and then, after washing, the plate is immersed in the fixing bath. The solution acts very vigorously, and should be diluted if only a small reduction is required. Local reduction may be effected by using a paint brush charged with this solution on the moistened film. This practice is not, however, much to be recommended, as it is rather working in the dark.

Density may also be diminished by the use of a strong solution of cyanide. Local reduction may be given by moistening the parts required to be reduced with water by a paint brush, and then applying the cyanide in the same manner. The reduction can be seen progressing.

There are a variety of formulæ extant for reducing negatives. Perhaps the best is eau-de-javelle, which can be obtained of all chemists, but which is made as follows :—

| | | | |
|----------------------|-----|-----|----------|
| Dry chloride of lime | ... | ... | 2 ounces |
| Carbonate of potash | ... | ... | 4 " |
| Water ... | ... | ... | 40 " |

The lime is mixed with 30 ounces of the water, and the carbonate dissolved in the other 10 ounces. The solutions are mixed, boiled, and filtered. The filtering solution should be diluted, and the plate immersed in it till reduction takes place. The plate should be fixed, and again washed.

Yellow Stains.—Usually a yellowish veil appears to dim the brightness of the shadows when the development has been effected by the alkaline developer. This may be

removed, if thought requisite, by the application of one or two drops of hydrochloric acid to an ounce of water, and floating it over the surface of the plate. This must be done after the negative has been freed from hyposulphite, otherwise the acid decomposes this salt, and there is a deposition of sulphur. Mr. Cowell has recommended another clearing solution, which is made as follows:—

| | | | | |
|-------------|-----|-----|-----|----------|
| Alum | ... | ... | ... | 1 ounce |
| Citric acid | ... | ... | ... | 2 ounces |
| Water | ... | ... | ... | 10 „ |

Mr. B. J. Edwards makes this solution sherry-coloured with ferric chloride, but we do not find any marked advantage in so doing. The film must be washed almost immediately, as the acid is apt to cause frilling.

Another formula is—

| | | |
|----------------------------|-----|---------------------|
| Saturated solution of alum | ... | 20 ounces |
| Hydrochloric acid | ... | $\frac{1}{2}$ ounce |

The negative should be well washed in all cases after the application of either of them.

Too Granular an Emulsion is usually due to bad mixing of the soluble bromide and the silver nitrate; but it may also be caused by over-boiling, and also by too small a quantity of gelatine in the boiling operation. Digesting too long with ammonia, as in Van Monckhoven's process, has the same effect. There is no cure for this evil.

Opaque Spots on a plate are almost invariably due to dust settling on the film when drying; they also may be due to imperfect filtering of the emulsion.

Semi-transparent Spots on the plate before development are generally due to (1st) defects in the glass plate, or (2nd) to the use of gelatine containing grease. We have found that the use of a substratum is a certain cure for these transparent spots.

As has already been pointed out, certain gelatines are apt to contain grease, and that so intimately that soaking

in ether or washing with ammonia will not eliminate it. A specific is as follows :—We will suppose that 80 grains of Coignet's gelatine are required : 90 grains are weighed out, soaked in water, drained, and melted. The liquid is then very slowly poured, almost drop by drop, into methylated spirit, free from resin, where it is precipitated in shreds of a white pasty character ; after it is all precipitated the spirit is poured off, and a slight rinse with fresh spirit given, and then it is covered with water, in which it should remain till the whiteness disappears. The water should then be changed, and the gelatine drained and redissolved ; about 10 grains out of the 90 seem to be dissolved in the mixture of alcohol and water. Emulsions made with this gelatine will be markedly free from grease spots. The same method may be adopted for large quantities of gelatine, omitting the final wash with water, and leaving it to dry spontaneously. This is best done on glazed dishes. The gelatine can be broken up, weighed, and used in the usual manner. Another plan is to soak the gelatine in water with a full quantity of water ; drain off what can be drained off, pressing the gelatine during draining. The gelatine is next melted, and to every 100 grains used $\frac{1}{4}$ ounce of strong ammonia is added. When set, the gelatine is squeezed through netting, and washed till an alkaline reaction is only just shown on red litmus paper. All grease is saponified and washed out to a great extent. The gelatine may be added to the boiled emulsion in the moist condition.

Dull Spots on the Negative are also due to the use of gelatine which contains greasy matter. They seem to be formed by the repellent action of the gelatine for the silver bromide. If a plate be carefully examined by daylight, the dull spots can be seen before development, and are seen to be placed where the surface is denuded of gelatine, and, there being no restraining action by the gelatine, these are first reduced by the developer. If a plate which shows such repellent action be coated with a

weak solution of gelatine or albumen, and then be dried, the evil will be much mitigated. These dull spots are usually met with in most aggravated form in hot weather, when the emulsion takes long to set, and, consequently, when the repellent action has longer to develop its power. In hot weather the slab should be cooled with ice to avoid this evil.

Fits are, in reality, an aggravated form of dull spots. The repellent action in this case is able not only to cause the gelatine to be repelled, but also to carry with it the bromide as well.

Want of Density in a negative may be caused by over-exposure, but it more often arises from the emulsion itself.

A rapid emulsion has a tendency to give a feebler image than a slow emulsion, although to form the image the same amount of silver may be reduced. This shows that the silver is in such a state of aggregation that it does not possess what may be called covering powers. We have found that the addition of a chloride emulsion materially aids the production of density. If one-fifth part of an emulsion prepared according to Chapter XXV. be added to an emulsion lacking density-giving qualities, it will be secured without detriment to the sensitiveness. The range of sensitiveness will be slightly altered. A hard gelatine is also conducive to feeble images. If prepared plates give feeble images, resort must be had to intensifying.

Irregular-shaped Spots, which refuse to develop, are often caused by the use of chrome alum in emulsions which contain free alkali. Ammonia causes a precipitate with chrome alum, and this encloses particles of bromide, and prevents the action of the developer upon it.

Transparent Pinholes on the Negatives after Fixing may arise from minute air-bells in the emulsion, or from dust which finds its way into the slides or changing-box. The former disappear if the emulsion is kept before coating.

The latter can be avoided by rubbing the dark slides with a minute trace of glycerine. This acts as a trap for the dust, and prevents its finding its way on the plates.

Dark Scratches on the Negative.—Sometimes plates on development show dark scratches, which appear unaccountable. If the plates have been rubbed together, or if any grit has been rubbed on them, this will account for the markings.

CHAPTER XXXII.

COLLODION EMULSIONS—(INTRODUCTORY).

A GREAT variety of formulæ for collodion emulsions have been published at one time or another. It would be impossible to give all which have from time to time been given in the various photographic publications, but a selection has been made of what the writer conceives to be the most successful; at least, which have proved most successful in his hands.

These may be divided into two classes: one, in which the emulsion is formed in collodion, and the plate coated and then washed; the other, in which the same emulsion is dried and washed, and re-dissolved, the plate being coated with the emulsion as required. With the former method, unless the bromide is in excess, the emulsion has to be prepared from time to time as required, and if the bromide be in excess, the emulsion works very slowly. With the latter process, where it is washed, the emulsion will keep any time, always supposing no decomposition sets up in the pyroxylin. We have ourselves kept some emulsions of this class seven years which are just as sensitive, if not more sensitive than when freshly prepared.

The plain collodion with which the emulsion is to be

made shall be first dealt with, distinguishing the qualities necessary for the unwashed and for the washed emulsion.

Some emulsion workers have laid it down as an axiom that the pyroxylin for the two processes should differ, while others declare that this is unnecessary. Again, some declare that to gain good density the pyroxylin should contain a percentage of organic matter, presumably to be capable of acting on the silver bromide during development, or by forming some definite compound with silver. Our own experience is, that for securing density, organic matter is unnecessary, though it may improve sensitiveness; and we have found in some instances that density was absolutely impossible to attain where organic matter was present. We shall touch on the question of density of the image further on.

If a preservative be used as a sensitizer, there can be no doubt that a collodion should be used which is as porous as possible, to enable it to surround the particles of the sensitive salt. This porosity has also another advantage, which is, that when the preservative is washed off previous to development, the sensitive salt is immediately accessible to the action of the developer. It is such a collodion that is recommended for dry plates prepared with the aid of the bath, more particularly in the collodio-albumen process, though in this process the sensitive salt is more especially contained in the albumen, and it is therefore necessary that a fair quantity of the latter should be on the plate, which is accomplished by this porosity of the collodion film. For any emulsion process, we consider a horny collodion objectionable, owing to the difficulty that exists in making the developer penetrate through the film. A horny collodion has, however, one advantage in that it acts as a varnish to exclude the air from the sensitive salts enclosed within it. In the following formulæ which are given for the preparation of the pyroxylin, one will produce an ordinary tough film, and

the other a fairly porous film, and consequently a rather powdery pyroxylin.

The solvents of the pyroxylin should be as pure as practicable to secure the maximum of sensitiveness. There is, for instance, no doubt that when methlated alcohol is used, there may be a lack of sensitiveness, and even a production of fog. The ordinary methylated ether, however, will be found, as a rule, to be sufficiently pure.

CHAPTER XXXIII.

PYROXYLIN.

THE following formulæ for the preparation of the various kinds of pyroxylin will be useful to note. The first is taken from "Instruction in Photography," and is reprinted here as being convenient for reference. The general directions given are those recommended by Hardwich. Take—

| | |
|-------------------------------------|---------------------|
| Sulphuric acid (1·842) at 15° Cent. | 18 fluid ounces |
| Nitric acid (1·456) | 6 " " |
| Water | 4 $\frac{3}{4}$ " " |

Or,

| | |
|-------------------------------|---------------------|
| Sulphuric acid (1·842) | 18 fluid ounces |
| *Nitric acid (1·42) | 6 $\frac{1}{2}$ " " |
| Water | 4 $\frac{1}{4}$ " " |

The water is first poured into a strong glazed porcelain basin, the nitric acid next added, and lastly, the sulphuric acid. The mixture is well stirred with a glass rod. The temperature will now be found to be somewhere about 190°. It must be allowed to cool to 150°, and this tem-

* The nitric acid of the strength given in this formula is cheaper than that of the first, and is a standard strength, hence it is recommended for economy's sake to use it.

perature must be maintained on a water bath. A dozen balls of cotton-wool, weighing about thirty grains (which have previously been well washed in carbonate of soda and thoroughly dried), should now be immersed separately in the fluid with the aid of a glass spatula. Each ball should be pressed separately against the side of the basin, till it is evident that the acids have soaked into the fibre. Care must be taken that each one is immersed at once. Failing this, a different chemical combination takes place, and nitrous fumes are given off, and the success of the operation is vitiated. Immersing the dozen balls will take about two minutes. The basin should after this be covered up for about ten minutes.* At the expiration of this time the whole of the cotton should be taken up between two glass spatulas, and against the sides of the clean porcelain capsule as much of the acids as possible should be squeezed out. The cotton should then be dashed into a large quantity of water, and washed in running, or frequent changes of, water for twenty-four hours. Finally, when it shows no acid reaction to blue litmus paper, it is dried in the sun or on a water-bath.

The operation may be conjectured to be successful if the cotton tear easily in the hand, and if the original lumps cannot be easily separated. Should nothing but fragments of the lumps be detected, it is probable (if the acids used have been of the strength given above) that the temperature has been allowed to fall. If dried, the pyroxylin should, when pulled, break up into little bits, and should not resemble the original cotton in texture.

The weight of good pyroxylin should be greater than the original cotton by about 25 per cent.

If the acids used are too strong, the pyroxylin will be much heavier than this percentage, and will make a thick glutinous collodion; whereas, if the acids have been too

* This prevents the access of the air to the fluid, and prevents the absorption of oxygen, and consequent formation of the nitrous fumes.

diluted, it will probably weigh less than the original cotton, and will yield a collodion adhering firmly to the plate, and giving negatives of too great softness; any small particles of dust that may fall on the glass will form transparent marks. The formula given steers between the two extremes. There is a large proportion of sulphuric acid in the above solution of acids, and it is to this that is probably due the tough film which the resulting collodion gives. In fact, the excess of sulphuric acid partially "parchmentizes" the cotton.

The late Mr. G. W. Simpson described a modification of Hardwich's formula, which has given excellent results in our hands; the mode of procedure is the same as that described above. "As Hardwich's formula for the manufacture of pyroxlin is given, we may add a caution derived from our own experience with it. In our practice, we found it to contain too large a proportion of water, and our experiments with it issued in something like fifty per cent. of failures, the cotton dissolving almost entirely in the acids. We may add a formula which we have found to give an excellent sample of soluble cotton for emulsion work, the collodion holding the particles of silver salt well in suspension, and giving a homogeneous film, adhering well to the glass. The formula we subjoin has the advantage that the acids are readily obtainable in commerce of the strength we mention, and are consequently cheap. Six measured parts of sulphuric acid 1.840 (ordinary commercial oil of vitriol will serve), and four measured parts of nitric acid 1.360. This is the strength of acid commonly sold as a pure nitric acid. In three measured ounces of the mixed acids, one drachm of cotton wool should be immersed at a temperature of 150° Fah., using a water bath to maintain that temperature for ten minutes, when the cotton should be removed and washed at once in a large quantity of water."

In the next formulæ the proportion of sulphuric acid is diminished, and in consequence we get a pyroxlin which

is, if anything, deficient in tenacity. For dry plate processes with the bath, however, it is excellent, and will be found of great use in emulsion processes in which a preservative is used. The formulæ are those given by Warnerke in a communication to the Photographic Society of Great Britain made in 1876.

His *modus operandi*, based on a communication made to him by Colonel Stuart Wortley, is the following:—100 grains of the finest cotton-wool are put into a porcelain jar, and 30 grains of gelatine dissolved in the smallest amount of hot water are added. By pressing it with a wooden stick, all the cotton will be uniformly impregnated. It is subsequently very thoroughly dried before the fire.

| | | | |
|--------------------------------|-----|--------------|--------------|
| Nitric acid (sp. gr. 1.450) | ... | 4 | fluid ounces |
| Water... | ... | 12½ | drachms |
| Sulphuric acid (sp. gr. 1.840) | 6 | fluid ounces | |

are mixed in the order named. An arrangement is provided to keep the temperature of the mixture uniformly at 158° Fahr. The dried gelatinized cotton, weighing now about 130 grains, is immersed in the mixed acids, and left in twenty minutes. After the lapse of this time the acids are pressed out, and the pyroxylin quickly transferred to a large vessel of water. Washing and drying follow. Colonel Stuart Wortley recommended also a second mode. Gelatine, instead of being added to the cotton, is dissolved in the water figuring in the formula of the acids, and ordinary dry cotton immersed in the mixture of gelatinized acids.

Mr. Warnerke states that before washing the gelatinized emulsion a remarkable increase of intensity and sensitiveness is obtained. After washing, the difference is less striking, but still sufficiently marked to prove the new pyroxylin to be a very decided improvement.

Mr. Warnerke states that pyroxylin giving extraordinary density can be prepared from the raw hemp. Colloid from hemp-pyroxylin is red in colour, and very fluid;

but the insoluble deposit is very considerable ; it also requires stronger acids. It is worth remarking that the strength of acids must vary with different samples of fibres, even in the case of different cottons. A very good pyroxylin can be prepared from Whatman's hand-made paper, instead of the cotton in the above formula, which, being sized with gelatine, offers a ready-made material, suitable for making gelatinized pyroxylin."

The great difficulty in this formula is the easy solubility of the cotton at the high temperature. A reduction in the amount of water will prevent this. *Pyroxylin from ungelatinized cotton can be prepared by the same formula,* and gives a powdery film. The writer disagrees with Mr. Warnerke as to the desirability of this state of the film for washed emulsion when used on rigid supports, such as glass, but the limpidity given by it to the collodion is very desirable in the case of a flexible support, such as that with which Mr. Warnerke's name is associated.

Mr. W. B. Bolton gave an excellent description of the method to be adopted for making any pyroxylin suitable for emulsion. He says :

"Pyroxylin possessing the requisite qualities is by no means so easily obtained as the ordinary sort. Precipitated pyroxylin forms at once, if properly made, even from the cheapest materials, not only a perfect substitute for the high-priced samples usually employed, but for some purposes gives an absolutely superior result.

"We commenced with a sample of pyroxylin which is sold at 16s. the pound ; it is very soluble, and gives little or no residue, but is of little use for emulsion work. Of this, 400 grains were dissolved in a mixture of 10 ounces of methylated ether, s.g. .730, and 10 ounces of ordinary methylated spirit, retailed at 5s. a gallon. The resulting collodion, after standing for a couple of days, though very thick, as might be expected, was tolerably clear, except for the presence of a few floating specks and particles of

dust, which were removed by passing it through muslin. This was poured into cold water, and the precipitate, when washed and thoroughly dried, weighed 368 grains, or exactly 8 per cent. less than the original cotton."

After stating that it is a wrong plan to pursue to pour the collodion gently on the water, the writer continues :

"The proper course to follow, as laid down by M. Chardon, is just the reverse of this; the collodion is poured into the water in a thin stream—preferably from a height—and is stirred vigorously during the time of pouring, and for a minute or two afterwards. By this means it is broken up into innumerable drops, each of which, immediately it comes into contact with the water, is converted into a distinct spongy mass or flock, being deprived almost instantaneously of its ether and alcohol. The stirring is continued as long as the mass exhibits any cohesive tendency, and when it feels harsh and firm to the touch, it may be known that the removal of the solvents is complete. The water is then changed, the cotton passed through a cloth, and dried.

"Except in physical conditions, we cannot find, with a given sample of cotton, that it is of much importance whether the precipitation is performed in hot or cold water."

In order to avoid waste in washing and drying, it will be found convenient to employ a conical bag fixed upon a hoop of thin cane. When the precipitation is complete, the whole of the contents of the vessel are transferred to the washing bag, and after passing two or three pints of water through to remove the last traces of ether and alcohol, the mass of cotton is squeezed as dry as possible, and may then be removed as a lump; it is then broken down with the fingers or a spatula upon a clean porcelain dish, and dried at a gentle heat on a warm bath. When quite dry, it should present the appearance of light flakes of pure white, and easily reduced to powder. It dissolves as rapidly as ordinary pyroxylin, and, if carefully

prepared, gives at once a perfectly bright solution of a faint yellow tinge. It gives upon the glass a hard, smooth film, non-contractile, and yet differing totally from the so-called powdery films commonly spoken of in connection with dry plates.

In the same article, a reference is made to M. Blondeau's analysis of precipitated cotton, in which it is stated that 8 per cent. of water is taken into combination. This amount of water, if it exists in the cotton, must alter the structure of the collodion in a marked way.

Be this as it may, precipitated cotton does give a very fine film; but we are inclined to think that part of the effect is produced by the alcohol being eliminated from it *en masse*, and carrying with it that constituent of the pyroxylin which is soluble in the alcohol. This will be seen to be the case in which a finished emulsion was washed in alcohol; the resulting film having much resemblance to that of M. Chardon's.

The amateur will probably find it most convenient to purchase ordinary pyroxylin from some respectable dealer, who is a manufacturer of good collodion, instead of making it himself, for, of all processes connected with photography, that of making pyroxylin is, perhaps, the most unpleasant and hurtful to the health and clothes. The stains on the latter from nitric acid or sulphuric acid can never be eliminated, unless the acid be immediately neutralized, and sulphuric acid will rapidly eat through any organic texture, unless it be either washed *thoroughly*, or an alkali be applied.

As regards the character of the solvents, there is little to be said in regard to the ether. That of a specific gravity of $\cdot 730$ is generally employed, and, if it be, an alcohol of low specific gravity should be employed, such as $\cdot 812$; whereas if the ether have a specific gravity of $\cdot 720$, a specific gravity of $\cdot 820$ for the alcohol is allowable.

After the plain collodion (see next page) is mixed, it should be allowed to settle. No matter what pyroxylin

be employed, it will invariably be found that there is some flocculent matter, too fine for filtering out, which, if not got rid of, is one great cause of spots on emulsion plates, and therefore every effort should be made to prevent its finding its way into the emulsion. The collodion should, therefore, be allowed to remain undisturbed for a week or two, to allow these fine particles to deposit.

CHAPTER XXXIV.

PREPARATION OF AN EMULSION.

It is unnecessary to enter into the history of the emulsion processes; but it may not be uninteresting to note that the first published formula for a collodio-bromide emulsion was by Messrs. Bolton and Sayce, in September, 1864.

Though not following an historical order, we have thought it best to give the method of preparing an emulsion which can be followed in nearly all modifications of the process; and to make it clearer, a definite formula has been made use of, giving an emulsion which is very simple and clean working, and though not boasting any extraordinary sensitiveness, is yet more sensitive than any bath dry-plate process with which the writer is acquainted.

The plain collodion* is made as follows:—

| | | | | | |
|----------------------|------|-----|-----|-----|------------|
| Alcohol | ·820 | ... | ... | ... | 10 ounces |
| Ether | ·730 | ... | ... | ... | 20 " |
| Pyroxylin (ordinary) | ... | ... | ... | ... | 400 grains |

* If the plain collodion supplied by dealers be used, it must be recollected that, as a rule, it contains about 5 grains of pyroxylin to the ounce after the iodizer has been added. The formula may be taken to be as follows:—

| | | | | | | |
|-----------|-----|-----|-----|-----|-----|------------|
| Alcohol | ... | ... | ... | ... | ... | 20 ounces |
| Ether | ... | ... | ... | ... | ... | 40 " |
| Pyroxylin | ... | ... | ... | ... | ... | 400 grains |

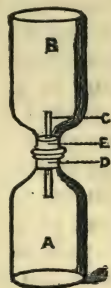
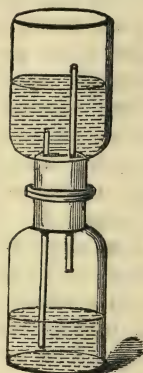
The bromide and silver must be added *according to the grains of pyroxylin, not according to the amount of solvents in which it is dissolved.*

We will suppose that we are going to prepare an emulsion which will make up to twenty ounces. When it is evaporated, washed, and re-emulsified, each ounce of washed emulsion should contain about 5 grains of pyroxyline, and, therefore, we must take one-fourth of the collodion made up as above (*vide* Note page 218), which will be $7\frac{1}{2}$ fluid ounces. It is proposed that each fluid ounce of re-dissolved emulsion shall contain about 15 grains of silver bromide. The salt we propose to use is zinc bromide, and we find that about 10 grains of this salt are necessary for this purpose. To our $7\frac{1}{2}$ ounces of collodion, therefore, we must add at some time or another 200 grains of this salt. Two portions of 100 grains each are weighed out: one is dissolved in the smallest quantity possible of alcohol, and 4 or 5 drops of concentrated nitric acid are added to it to render innocuous any oxide or other impurity that may be present. This is then added to the collodion. The other 100 grains are similarly dissolved, but a larger proportion of nitric acid added, viz., 10 drops. This is kept in a test-tube ready for use. We next require 300 grains of silver nitrate to saturate the zinc-bromide, and to allow 3 grains in excess for each ounce of the concentrated collodion. As this will probably be about 11 ounces by the time the additions are made, 330 grains of silver nitrate (which has previously been pounded up in an agate mortar, or the crystals of which have been crushed with a glass stopper on a thick glass plate) are weighed out. This amount is then placed in a large test-tube, with 5 dr. of water, and warmed: a perfect solution ought to result. Ten drops of nitric acid are next added to it. In another test-tube $1\frac{1}{2}$ ounces of alcohol (820 to 830) are boiled, and poured upon the dissolved silver. The two fluids may not mix at first, but by pouring them from one test-tube to another this is readily accomplished. The collodion is now placed in a glass jar, and a stirring-rod placed ready to hand. It is usually insisted that the subsequent operations should be conducted in the dark-

room. This exclusion of light is quite unnecessary (as the writer has practically proved), owing to the presence of the nitric acid, which renders the sub-bromide inert as fast as it is formed by the action of light. The test-tube containing the silver is now taken in the left hand, and the stirring-rod in the right, and three-quarters of the silver nitrate solution is poured, drop by drop, into the collodion, which is kept in brisk agitation by the glass rod. The silver solution is then placed on one side, and the dissolved bromide solution taken in the left hand. All the latter is now added drop by drop, and then the remainder of the silver solution in a similar manner. Some of the silver salt is sure to be found crystallized on the edge and sides of the test-tube. This is re-dissolved, as before, in a little water and half an ounce of alcohol, and added with the same precautions. If the above details have been carefully carried out, the colour of a candle or gas-flame, when viewed through the liquid which runs down the inside of the glass jar after agitation, should appear of a deep orange approaching to a ruby tint. When in this condition, it may be judged that it has been rightly prepared. With the glass rod a drop or two of the emulsion should be dropped on to small strips of glass, and examined by daylight for structure, &c. When viewed through a window, the principal part of the light transmitted should be orange. A little potassium *chromate* should be dropped on to the emulsion on the plate, and a bright red colour will show that the silver is in excess, which is what is required in our case. If this colouration be absent, it will indicate that the soluble bromide is in excess, which, in some modifications of the same process, is what may be desired. The emulsion must next be decanted off into a bottle capable of containing at least double the amount of fluid—that is, at least 20 ounces—and it should then be shaken for ten minutes. It may now be put on one side for from sixteen to twenty-four hours, when it will be ready for the next operation.

We will now give a slightly different method for mixing the silver and the soluble bromide, which has been adopted by some people, amongst others by Warnerke, to whom the writer is much indebted for information on various points.

A couple of corks, D and E (fig. 26), which should fit the necks of the bottles A and B, are bored with holes just wide enough to admit a glass tube, C, which has a diameter of bore of about one-eighth of an inch. The whole of the bromide is dissolved in half the amount of collodion used, and placed in the bottle A, which (like B) should have sufficient capacity to hold double the amount of emulsion to be made up; the cork, D, with the glass rod, C, should

*Fig. 26.**Fig. 27.*

next be fitted into it. Into the other bottle, B, the silver nitrate solution is added to the collodion, sufficient alcohol and water being used to keep it in thorough solution. The bored cork, E, is then fitted in the neck, and the far end of the glass tube deftly inserted, and the tops of the bottles brought close together. The hands then grasp the necks, and the contents are shaken up, when a little of B gradually finds its way into A. The positions of the bottles are

then reversed, and a little of the contents of A shaken into B; when each of the bottles seems to contain emulsion equally dense, the whole of one bottle is gradually caused to drop into the other, and by this means a perfect emulsion is obtained. The emulsion may be made even more rapidly by adopting the contrivance shown in fig. 27, in which there are two tubes, one always acting as an inlet for air, whilst through the other the collodion finds a passage. In this case, narrow bored tubes are advisable, certainly not greater than one-eighth of an inch.

Now it has been said that in sixteen to twenty-four hours the emulsion will be ready for pouring out. This statement is true for the particular emulsion described, but it is not necessarily true for emulsions when other soluble bromides are employed. Thus we find that Col. Wortley stated to the Photographic Society of Great Britain, on 14th March, 1876, that the following is the time necessary for emulsions made with the following soluble bromides to ripen:—

| | | | | | |
|------------|-----|-----|-----|-----|-------|
| Manganese | ... | ... | ... | 7½ | hours |
| Cadmium | ... | ... | ... | 9 | " |
| Strontium | ... | ... | ... | 10 | " |
| Magnesium | ... | ... | ... | 10 | " |
| Zinc ... | ... | ... | ... | 10½ | " |
| Cerium... | ... | ... | ... | 14 | " |
| Potassium | ... | ... | ... | 14 | " |
| Cinchonine | ... | ... | ... | 15 | " |
| Sodium | ... | ... | ... | 15½ | " |
| Calcium | ... | ... | ... | 17 | " |
| Ammonium | ... | ... | ... | 17½ | " |
| Uranium | ... | ... | ... | 17½ | " |
| Barium... | ... | ... | ... | 19 | " |

It will be noticed that Colonel Wortley gives zinc emulsion ten and a-half hours, as the time for attaining the maximum sensitiveness. The discrepancy is probably due to the greater viscosity of the collodion employed in

the one case as compared with the other. The list, however, is useful as showing the comparative times that should be allowed for ripening. We might here leave the emulsion as ready for coating plates after proper dilution, but we will further suppose that it is to be washed, a modification introduced by Mr. W. B. Bolton, one of the originators of the collodio-bromide emulsion process. The first step to be taken is to allow the solvents to evaporate.

Evaporating the Solvents.—An emulsion generally may be prepared in the afternoon of one day, well shaken before leaving the laboratory, and on the next day, about noon, the emulsion will be ready for drying. The mode adopted by the writer is as follows:—The emulsion is poured out into a flat dish, to a depth of a quarter of an inch, and placed in a dark room, the temperature of the latter being raised, if possible, to 70°. For the ten ounces of emulsion made, a porcelain dish, about 14 by 12 by three-quarters of an inch deep, is required.

After a short interval it will be found that a skin forms on the surface of the collodion; this is broken up with a glass rod, and a fresh liquid surface given to it. Every half hour the whole of the emulsion is thoroughly well stirred up, till it begins to break into lumps, when it can be left a short time, for the solvents still further to evaporate. It is ready for the first washing when the lumps require a little force to break them up—in other words, when they are about the same consistency as a collodion film before dipping into the bath. The mass is then removed to a glass beaker, and covered with distilled water. At this point we have a good test as to whether the evaporation of the solvents has been continued far enough. If only a few of the lumps rise to the surface, the evaporation has been sufficient; if, on the other hand, the majority float on the surface of the water, it has not been continued long enough. The reason of this tendency of the lumps to rise to the surface is due to the

light specific gravity of the ether and alcohol, which, even with the weight of the solid matter, is not sufficient to counterbalance the specific gravity of the water.

This method of eliminating the solvents is, however, wasteful, and, if preferred, resort may be had to distillation; but this method should not be adopted *unless all acid be omitted* previous to distillation, since boiling an emulsion in its presence produces a very horny film, and nitrous ether is formed. The acid must be applied in the first wash water. Let it be recollected that where the bromide is not in excess, *but where there is an excess of silver nitrate, nitric acid, or its equivalent, must be added to the emulsion itself, or to the wash-water*, at some stage—the time of addition being dependent on the circumstances already explained. *The whole of the operations up to the first washing may be carried on in the light.* In M. Chardon's process, as subsequently given (page 230), it will be seen how this evaporation of the solvents, previous to washing, may be dispensed with. It is hardly worth while to repeat the method here, more particularly when, in some respects, the above is really superior to it; at least, so the writer has found.

For the above quantity of emulsion, 1 drachm of nitric acid, which will be ample to secure freedom from fog, should be dropped into the dish, and distilled water added. After a couple of hours the true washing may commence.

A method which we have found to give still better results, if the acid is omitted from the emulsion, is to wash the pellicle twice or three times in water till nearly all excess of silver is removed, and then to add 2 drachms of hydrochloric acid to the next wash-water (which should not be more than ten ounces), and then begin to wash *de novo*. Mr. W. Bedford first recommended this plan. Instead of the hydrochloric acid, a solution of bichromate of potash, ten grains to the ounce, to which a pinch of common salt has been added, may be substituted. This is an excellent method, since any trace

of bichromate is visible in the wash-water. The pinch of salt prevents the formation of bichromate of silver.

To wash the emulsion, it may be placed in a jar or jam pot, and be covered with water, where it can stand two or three hours in the dark without detriment, when it should be changed. The way in which the washing can be economically effected, as regards time, is at follows:—A piece of course calico which has previously been washed in carbonate of soda, and then well rinsed, and dried, is spread over the top of a second glass jar or large jam pot, and the contents of the first thrown on to it. The calico acts as a strainer, and the solid pellicle is left on it. The calico is next taken up by the sides, and the contents are twisted up in it, and as much as possible of the liquid then wrung out. The calico is untwisted, and a bag formed by tying up the ends, to holds the emulsion, which is shaken up and immersed in fresh distilled water. After a quarter of an hour the wringing operations are again proceeded with, and this process repeated three or four times. The expelled water should now be tested for free silver nitrate by a drop of hydrochloric acid. If it gives more than a slight milkiness, such as is produced by adding silver nitrate to water containing a grain of common salt to the gallon, it must be washed till this maximum is attained.

Preparing the Pellicle for Re-emulsifying.—A very important part of emulsion making is now to be touched upon, viz., getting rid of the water held in the pellicular mass.

To commence with, as much water as possible should be squeezed out, and then we may proceed in one of these ways.

1st. We may lay it out flat on a piece of blotting-paper, and allow it to dry spontaneously. 2nd. We may put it in a flat porcelain dish, and place it in a water bath, the temperature of which can never exceed 150° , and thus all moisture may be got rid of. In this proceeding the very greatest care is necessary, as the emulsion is apt to

become very hard indeed—so much so as to be scarcely soluble; in addition to which, it is often apt to blacken spontaneously if the temperature be at all high. The third method is one which we can confidently recommend for washed emulsion, being very simple, and absolutely improving its qualities when re-dissolved. This is to cover it with rectified spirit '820 after as much water as possible has been squeezed out of it. In an hour's time the excess is drained off, and the pellicle is squeezed in the cotton rag as before. It is then once more covered with the spirit, and left for half-an-hour, when, after draining away the superfluous spirit, it is ready for re-emulsifying. If it be desired to keep the pellicle in a solid state, it will only be necessary to expose it to the air for a few hours, when it will be found quite dry.

It is instructive to examine the washings from the spirit. It will be found that there is a certain small quantity of silver bromide in suspension, which can be filtered out. If the spirit be distilled over, a semi-opaque liquid residue will be left, having a very high boiling point, a strong and very disagreeable smell, and containing some organic salt of silver, which discolours in the light. It may be said that this organic compound is necessary for density of image; but a trial of the emulsion washed in this way will prove the contrary; in addition to which, it will be found much freer from spots than that washed and dried by the first two methods indicated above.

There are some pyroxylics which it would be dangerous to treat in this manner, since they are soluble, to a certain extent, in absolute alcohol; but it seems to the writer that any such pyroxylics are to be avoided when washed collodio-bromide emulsion is in question. If they are employed, the old method of drying must be adopted.

The dried (or moist with alcohol) pellicle has next to be dissolved in its proper proportions of solvents, which are about 5 grains of pyroxylin to every ounce of the two

when mixed. It is better to make it up first to the strength of 10 grains of pyroxylin, and then to add the remaining solvents, since the colour of the emulsion seems to be better when a greater degree of viscosity is present when the pellicle begins dissolving. In two or three hours the whole of the silver bromide should be in suspension. It will be found, however, that there is an improvement in the quality of the film after the lapse of a couple of days, or even more. A plate should be tried, before diluting down the collodion with more ether and alcohol, in order to test its flowing qualities, and to note the opacity of the film.

In our own experience we like to be able to see the outline of the flame of a gas jet through a film whilst moist, but which, when dried, obstructs it. In this condition the film is tough, requires no backing except for special purposes, and is always capable of giving sufficient density by alkaline development alone, without resort to intensification.

Before taking into use, the emulsion should be filtered through cotton-wool (see Chap. XVI.)

The exposure necessary for the washed emulsion already described is very constant; with a lens of aperture $\frac{f}{20}$, and in a fair light, thirty seconds will be found to be ample when using the alkaline or ferrous oxalate developer.

CHAPTER XXXV.

CANON BEECHEY'S PROCESS—M. CHARDON'S PROCESS.

Canon Beechey's Process.—We have now to put on record an unwashed collodion emulsion process, which is at once simple and efficient, and the thanks of the photographic public are due to Canon Beechey for its explicitness in every detail. The following is the *modus operandi*:—

| | |
|----------------------------------|------------------|
| Take cadmium bromide (anhydrous) | 400 grains |
| Alcohol (.805) | 10 ounces |

and allow the mixture to stand. Decant carefully, and add 80 minims of strong hydrochloric acid.

| | |
|-------------------------------|----------------------------|
| Take of the above solution... | $\frac{1}{2}$ ounce |
| Absolute ether (.720) | 9 drachms |
| Pyroxyline (as above) | 10 to 12 grains |

To sensitize this, dissolve 40 grains of silver nitrate in an ounce of alcohol (.820 sp. gr.) The best method of effecting this is to pound up the silver nitrate in an agate mortar, and to take only a quarter of the alcohol, and boil it in a test-tube containing the silver salt. The alcohol will become slightly brown (due, probably, to the formation of a fulminate of silver), and should be decanted off into a bottle containing the collodion. The

remaining silver should be dissolved up in a similar manner, the ounce of alcohol being just sufficient to effect solution.

Between each addition of the silver nitrate the collodion should be well shaken. When the final addition is made, the emulsion should be very smooth, and rather thick. When poured upon a strip of glass plate, it will appear transparent by transmitted light, but after keeping twenty-four hours (occasionally shaking the bottle containing it in the interval) it ought to be very opaque and creamy.

The plate is coated with a substratum, or edged (see Chap. XIX.) by running a camel's-hair brush one-eighth of an inch round the edges of the plates, with any of the substrata given in the same chapter. The collodion, which should have been shaken about half an hour* before, is poured on it in the ordinary manner, and, when set, immersed in a dish of distilled or rain water. When all greasiness has disappeared, it is flooded with any of the preservatives given in Chap. XLI. Canon Beechey recommends the plate to be immersed in a dish containing beer to which 1 grain per ounce of pyrogallie acid has been added. The drying is conducted in the usual manner. The exposure may be taken to be about twice that which is necessary for a wet plate. Between exposure and development the plate will keep fairly for a week, but after that it seems to lose detail, and appears under-exposed.

M. Chardon's Process.—The following process was awarded a prize by the French Photographic Society. It does not differ much from the first process given, except in the details of preparing the collodion.

In preparing the collodion for this process, M. Chardon prefers the use of two kinds of pyroxylin, both of which have previously been precipitated from collodion into

* Canon Beechey recommends the bottle to be shaken immediately before use, and the emulsion filtered.

water (see page 216). The one pyroxylin is prepared in the manner given at page 211; the other, the high temperature cotton, prepared as at page 214. These are mixed in the solvents to form collodion. A salted collodion is made up as follows:—

| | | | | |
|--|-----|-----|-----|-----------|
| Alcohol | ... | ... | ... | 1 ounce |
| Ether | ... | ... | ... | 2 ounces |
| Double bromide of cadmium and ammonium | ... | ... | ... | 14 grains |
| Zinc bromide | ... | ... | ... | 14 " |
| Precipitated pyroxylin, ordinary | ... | ... | ... | 7 " |
| Precipitated pyroxylin, high temperature | ... | ... | ... | 28 " |

A stock of this is made, and, when settled, decanted off as required. It must not be filtered, as the evaporation of the solvents is said to cause a change in the sensitiveness of the finished emulsion, though we doubt it. The collodion is rendered sensitive in small quantities at a time.

The silver nitrate is finely powdered, the quantities being as follows:—

| | | | |
|----------------------------|-----|-----|------------|
| The above salted collodion | ... | ... | 1 ounce |
| Silver nitrate | ... | ... | 6.2 grains |
| Alcohol | ... | ... | 3 ounces |

The ordinary means already described are employed for forming the emulsion (see page 221). The emulsion is vigorously shaken in a bottle, and put aside for thirty-six hours to ripen. After this time has elapsed, about an ounce of pure distilled water is placed in a glass beaker, and a drachm of the emulsion poured into it; after agitating the mixture, it is filtered clear, which can be effected by passing it once or twice through the filter paper. This waste is tested for silver nitrate. A slight milkiness on the addition of a chloride is all that is allowable. If it shows no signs of free silver nitrate, more of the latter salt dissolved in alcohol is added to the emulsion, just to give the necessary milkiness. This emulsion thus formed

is next corrected by a collodion in which cobaltic chloride is dissolved, made as follows :—

| | | | |
|-------------------|-----|-----|-----------|
| Alcohol ... | ... | ... | 1 ounce |
| Ether ... | ... | ... | 1½ " |
| Cobaltic chloride | ... | ... | 60 grains |
| Pyroxylin | ... | ... | 12 " |

Of this he adds about 2 drachms to each 10 ounces of emulsion; as before stated in this work (page 21), all causes of fog are thus eliminated.

The novelty of M. Chardon's process is now to be explained. He takes the finished emulsion, and pours it in a fine stream into a large quantity of water. After stirring, the precipitated emulsion is filtered through a cloth, is washed carefully (the method indicated at page 22 will answer), pressed between folds of blotting-paper, and dried in the dark. This gives a flocculent powder of a clear yellow colour. To prepare the finished emulsion, the following is prepared.—

| | | | |
|----------------------|-----|-----|----------|
| Ether ... | ... | ... | 1½ ounce |
| Alcohol... | ... | ... | 1½ " |
| Precipitated quinine | ... | ... | 1 grain |

The precipitated quinine can be made from the ordinary sulphate of quinine by dissolving it in sulphuric acid, and then adding ammonia. The precipitate thus formed is employed.

The organic substance is first dissolved in the alcohol, and, after filtering, the ether is added. To this amount of solvents 17 grains of the dried powder is added. After some hours, when all is in solution, the emulsion is filtered through cotton-wool (see Chapter XL.) M. Chardon states that the quinine gives porosity to the film; but it seems more probable that it acts like some other organic matters—viz., prevents a tendency to fog.

The exposure for plates prepared by this process is stated to be about double that required for a wet plate.

CHAPTER XXXVI.

COLLODION EMULSIONS TO WHICH PRESERVATIVES ARE ADDED.

Dawson's Process.—The next process which we shall describe is one described by Dr. Dawson, in which an “organifier” is added to the emulsion, and leads up to the more complicated form recommended by Mr. Carey Lea. We are indebted to the *British Journal Almanac* for the formulæ, which are as follows:—

Collodion.

| | | | | |
|------------------|-----|-----|-----|---------------------|
| Pyroxyline | ... | ... | ... | 8 grains |
| Cadmium bromide | ... | ... | ... | 7 „ |
| Ammonium bromide | ... | ... | ... | 2 „ |
| Ether .725 | ... | ... | ... | $\frac{1}{2}$ ounce |
| Alcohol .810 | ... | ... | ... | $\frac{1}{2}$ „ |

In practice we have found no difference in result, if ether of .730 be used, and alcohol of .812.

In our experience we find that the collodion should be allowed to settle some days, and then be decanted off. The pyroxyline employed may be that given at page 21.

To sensitize this, a mixture is made of—

| | | | | |
|----------------|-----|-----|-----|-----------|
| Silver nitrate | ... | ... | ... | 13 grains |
| Acetic acid | ... | ... | ... | 2 drops |
| Glycerine | ... | ... | ... | 1 drachm |
| Alcohol .830 | ... | ... | ... | 4 drachms |

These are dissolved in the usual manner, it being, perhaps, the better plan to leave the glycerine out till the last minute. After emulsification it is allowed to stand twenty-four hours, and then 2 drops of hydrochloric acid are added to the above quantities. It is allowed to rest for another twenty-four hours.

The emulsion is poured out into a dish of sufficient capacity, in order for the solvents to evaporate, and in five or six hours it is ready for further treatment. This consists in covering the pellicular mass with water for an hour, and, after pouring off, covering it *for a similar time* with—

| | | | | |
|-----------------------|-----|-----|-----|-----------|
| Tannin ... | ... | ... | ... | 5 grains |
| Gallic acid ... | ... | ... | ... | 2 " |
| Acetic acid ... | ... | ... | ... | 2 drachms |
| Water (distilled) ... | ... | ... | ... | 1 ounce |

The washing is now commenced in a manner similar to that already described at page 225, till all traces of acid are removed, which can be tested by litmus paper. When all the water is wrung out, the emulsion is dried in a hot water bath, or spread out in a warm room on blotting-paper.

The mode of eliminating all traces of water by alcohol is not admissible in this case, as it would dissolve out the tannic and gallic acid which may be left in the pellicle.

To re-dissolve the pellicle, equal quantities of ether and alcohol are used, having the same specific gravity as that given above. Dr. Dawson recommends that it be soaked in the alcohol for twelve hours before adding the ether.

The development of the plates can be carried out by the strong alkaline development.

Carey Lea's Chlor-Iodo-Bromide Process.—In this process we have silver iodide emulsified with bromide and chloride, and, in some hands, it works well. The following description will show how the emulsion is prepared. The collodion is made thus—

| | | | | |
|-------------------|-----|-----|-----|-----------|
| Ether, .730 ... | ... | ... | ... | 4 drachms |
| Alcohol, .805 ... | ... | ... | ... | 4 " |
| Pyroxyline ... | ... | ... | ... | 8 grains |

The cotton may be any of those given in Chap. XXXIV. To every ounce of collodion the following are added:—

| | | | |
|-----------------------|-----|----|--------|
| Dried cadmium bromide | ... | 9 | grains |
| Ammonium bromide | ... | 2½ | " |
| Ammonium iodide | ... | 2 | " |

Directly before emulsifying, add—

| | | | | |
|------------|-----|-----|-----|---------|
| Aqua-regia | ... | ... | ... | 2 drops |
|------------|-----|-----|-----|---------|

The emulsion, with an excess of silver, is formed by adding 25 to 30 grains of silver nitrate; and after an hour's interval, 2 grains of cupric chloride or cobaltic chloride; 2 drops of hydrochloric acid may be substituted for either of these, or for the aqua-regia.

The emulsion may at first appear flakey, but after the addition of the chloride it is only necessary to shake well and leave it for twelve hours. On again shaking, the emulsion will be found perfect. It may be used before drying, or after drying. In the former case, any of the preservatives ordinarily used may be employed.

If it has to be dried, it is poured out into a dish, and left till it is in a leathery condition on the surface, after which a preservative is poured upon it. Any preservative will answer, but Mr. Lea recommends—

| | | | | |
|---|-----|-----|-----|-----------|
| Water... | ... | ... | ... | 6 ounces |
| Acetic acid | ... | ... | ... | 3 drachms |
| Solution of gum-arabic with sugar | 4 | | | " |
| Prepared albumen | ... | ... | ... | 1 ounce |
| Gallic acid (60 grains to 1 ounce of alcohol) | ... | ... | ... | 4 drachms |
| Tannin (60 grains in 1 oz. of water) | 2 | | | " |

The albumen is prepared by the addition of an equal bulk of water to the white of one egg, and clarifying with 12 drops of acetic acid.

The gum and sugar solution is made by mixing half-a-pound of gum-arabic and two ounces of sugar in 44 ounces of water, and adding 1½ drachms of carbolic acid.

The pellicular mass is then broken up, and it and the preservative are transferred to a large glass jar and left there twenty minutes. The preservative is then poured off, and the washing takes place as given at page 225.

Instead of drying the emulsion, it may be poured direct into the preservative, taking care that the latter is more than four times the bulk of the former. The washing in this case takes place by decantation in the usual manner. This last method is stated to give the most soluble pellicle. The pellicle is then dried in the oven or water bath, and is re-emulsified by taking for each three ounces of the original collodion—

| | |
|--------------|---------|
| Ether | 1 ounce |
|--------------|---------|

| | |
|----------------|-----|
| Alcohol | 1 " |
|----------------|-----|

| | |
|---|----------|
| Plain collodion (4 grains of pyroxy- line to the ounce) | 2 ounces |
|---|----------|

Shake well at intervals, and in a week it is ready for use. The plate is coated in the ordinary manner, and dried. The exposure is stated to be about equal to that of a wet plate.

CHAPTER XXXVII.

MR. H. COOPER'S COLLODIO-BROMIDE RELIABLE DRY-PLATE PROCESS.

MR. COOPER'S formula is as follows :—

“Prepare first a stock of plain collodion by dissolving 160 grains of ordinary pyroxylin* in six ounces of absolute alcohol and ten ounces ether. Good methylated alcohol will answer for these first solvents, as also ether s.g. 730, purchasable at 1s. 6d. per lb. Also make an alcoholic solution of zinc bromide, 80 grains to the ounce. Even after filtering, this solution will throw down a deposit upon keeping, and this must be carefully left undisturbed. To make 10 ounces of washed emulsion, take 5 ounces of the above collodion, and add to it one ounce of the zinc bromide solution, and 20 minims of syrupy lactate of ammonia.† Sensitize with 150 grains of silver nitrate, dissolved first in 80 minims of water, and then in 3 ounces of strong alcohol. Boil together, and add it to the bromised collodion at once. I attach importance to

* Mr. Cooper recommends the pyroxylin as prepared by Hopkin and Williams, as answering the purpose.

† “Small experiments made since this paper was first written go to show that a great gain in sensitiveness may be obtained by reducing the proportion of plain collodion. I have tried three ounces, and even two ounces, instead of the five, with the most encouraging results. I am indebted to a leader in the *British Journal* for the suggestion.”

the addition of the boiling solution, so as to raise the temperature of the mixture, and when only a small quantity (such as the above) is made, I take the precaution to wrap the bottle in a thick cloth to retain the heat as long as possible. On examining the portions just given, it will be seen that the silver nitrate is decidedly in excess, and that the alcohol is used in larger proportion than usual.

"Lactate of silver has long been a favourite addition of mine to emulsions, and I am more than ever pleased with its action. I must call attention to a curious effect which is produced if the bromised collodion is allowed to stand many minutes after the lactate is added, and before the sensitizing. The collodion becomes quite milky, and throws down a crystalline deposit. It is well to add the lactate immediately before the silver, or even to defer putting it in until after the sensitizing. I cannot pretend to say what chemical or physical effect occurs in the 'lactised' collodion: I merely mention the fact.

"The emulsion is ripe in about twenty-four hours; but I am disposed to think it an improvement to keep it for a longer time, up to three days. At the expiration of the ripening period, twenty minims of strongest nitric acid are to be added, and the emulsion well shaken. I prefer to add the acid just before the washing instead of at first. I believe a better film is given by so doing.

"We are now faced with the question of how best to wash the emulsion. Shall we pour it out and evaporate the solvents, or precipitate it? From a lengthened experience of both methods, I cannot recommend precipitation, except in cases where the finished emulsion is to be used up within a month. It is now a generally acknowledged fact that precipitated emulsions will not keep well. But where large batches of plates can be prepared at a time, and no waste occurs, I can speak to the good qualities of the emulsion when precipitated by mixing it with twice its bulk of the following organifier,

and when the pellicle has fully separated and set, washing for some time in water containing a little nitric acid (half-ounce to one gallon), and finally in several changes of pure water. The mixture—

| | | | |
|------------------------|-----|-----|------------|
| Tannin ... | ... | ... | 500 grains |
| Gallic acid ... | ... | ... | 200 „ |
| Grape sugar ... | ... | ... | 200 „ |
| Strong acetic acid ... | ... | ... | 10 ounces |

or a proportionately lesser quantity of glacial, to be dissolved in water, and make up to 100 ounces. This method is expeditious. The alternative, and, I think, the better plan, is to pour out the emulsion into a sufficiently large dish (1 ounce to 25 square inches, or say 5 ounces in a 12 by 10 dish). Evaporate the solvents more thoroughly than usual; in fact, the pellicle may be allowed to get almost dry. Wash first in water containing half an ounce of nitric acid in one gallon of water, and then in plain clean water for some considerable time. If the water in use is hard, distilled water should be used at first and lastly. Wash thoroughly. The extra drying of the pellicle and the large proportion of alcohol it contained will materially assist in shortening the time. When dry, dissolve the above quantity of pellicle in 5 ounces of pure absolute alcohol, and a like quantity of extra purified methylated ether, s.g. .720. An emulsion prepared in this manner with the lactate of ammonia will give excellent negatives, without further preparation, if the plates are used at once; but its subsequent treatment with alkaline albumen gives the especial qualities for which I had so greatly valued it. The plates are much quickened by the after treatment. This particular emulsion has its sensitiveness doubled, whilst some others are rendered slower.”

Mr. Cooper then describes gelatinizing the plates with gelatine and chrome alum as given at page 115. He says that small plates may have an edging only, but that he prefers giving them the full coating:—

"Coat with the emulsion. When well set, immerse in water. I myself use a grooved box, well coated with shellac, and when I have coated and immersed as many plates as I intend to prepare, I cover up the box and thoroughly ventilate the room, so as to get rid of all fumes of alcohol and ether before proceeding further. I see no reason why a tin box with removable grooved pieces, similar to the one sent out by the Autotype Company for developing chromotypes, should not answer. Of course it must be kept for the purpose alone.

"The plates are now to be flooded with the alkaline albumen, or dipped in a bath of it. In either case the albumen must be in contact with the film for at least a minute. The plate is then to be thoroughly washed, flowed with a preservative, drained, and dried. After backing, it is ready for the camera. The albumen may be prepared in bulk, either with whites of eggs, or with the pure dried preparation. Of the latter, dissolve 60 grs. in 3 ounces of water, and add 1 drachm of strongest liquor ammonia .880. If white of egg be used, first pour in a few minims of dilute acetic acid, and well stir. In two or three hours strain, and to each ounce add two of water and one drachm of liquor ammonia.

"For the 'preservative' I have tried a host of substances, and find the simplest of all to be the best—viz., a two-grain solution of gallic acid. For the sake of constant uniformity and certainty, I was anxious to discard from my formulæ all compounds of uncertain chemical constitution, such as beer, or even tea and coffee, or else I could, from my own experience, speak strongly in favour of a decoction of tea, made by boiling 1 ounce of compressed black tea in 4 ounces alcohol and 12 ounces water. One ounce of this is diluted with 10 ounces of water to form the final coating for the plate. It is of importance that the plates should be thoroughly dried, especially if intended for packing; as although these plates will stand exposure to a moist atmosphere better than

most others, any damp remaining in the films when they are stored away will be a source of future trouble."

Mr. Cooper recommends a full exposure in the camera for these plates. We have found that with a stop $\frac{f}{20}$, and in an open landscape and good light, thirty seconds are ample, but that three minutes may be given without detriment. Of the negatives produced by this process, Mr. Cooper says:—

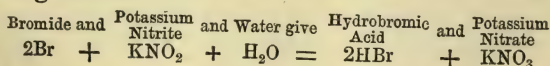
"First, the quality of image is almost perfect, much resembling that given by a really good collodio-albumen plate. Secondly, the films will keep for a lengthy period without deterioration, both before and after exposure. I exhibit a negative which was kept five months before exposure, remaining for three months in a dark slide, and carried about on long journeys, being submitted to many variations of temperature and hygroscopic conditions of the atmosphere. After exposure and before development it was kept five weeks. Other plates have been kept three months after exposure. I give these data, as many folks' ideas of a 'lengthy period' are various. I have plates prepared early this year which I am keeping on to test from time to time.

"In exposure, very great latitude is allowable—an unspeakable boon to the photographer on a tour, with no inconveniences for developing a trial plate from time to time."

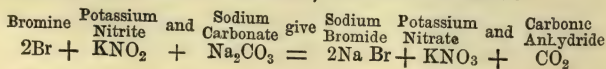
CHAPTER XXXVIII.

COLLODIO-BROMIDE EMULSION PREPARED IN THE ALKALINE STATE AND WITH EXCESS OF BROMIDE.

THE writer, in some recent investigations, was led to the conclusion that, theoretically, the loss of sensitiveness due to using a collodio-bromide emulsion with an excess of soluble bromide must be due to the want of a bromine absorbent; and that if, with an excess of soluble bromide, we had the presence of such an absorbent, that then the sensitiveness should be in a great measure restored. When light causes the liberation of bromine from the silver bromide (see page 9), and when a bromine absorbent, such as potassium nitrite, is present, we have the following reaction:—



The hydrobromic acid liberated would have a tendency to destroy the image; hence it is desirable that a neutral compound should be formed. This will be the case if an alkaline carbonate be added, for then we have—



This practically was proved to be the case. In making a washed emulsion with excess of bromide, it will be

well, then, to add to every ten ounces of emulsion two drachms of a saturated solution of potassium nitrite in alcohol, and to apply to the film sodium carbonate in the first wash water, and then to wash again. By this means the retarding effect of any trace of soluble bromide left is counteracted by the presence of the trace of potassium nitrite and of sodium carbonate.

The following formulæ will be found to form a very excellent emulsion, giving very beautiful films, which, for sensitiveness, are not behind those which are prepared with excess of silver nitrate. It is based on the alteration which is caused in the molecular structure of silver bromide by the use of ammonia, as adopted for the gelatine process. The ordinary collodion is formed as follows:—

| | |
|------------------------------|-----------|
| Pyroxylin (high temperature) | 25 grains |
| Alcohol | 2 ounces |
| Ether | 2 „ |

To this is added 100 grains of zinc bromide.

In order to emulsify this, 100 grains of silver nitrate are dissolved in the smallest possible quantity of water, made up to one ounce with alcohol, s.g. about .820, and liquor ammonia added, drop by drop, till the oxide first precipitated is re-dissolved. The emulsion is then formed as given in Chap. XXXIV. It is immediately placed in a dish to evaporate, when it is at once washed till it shows no alkaline, or a very faint trace of alkaline, reaction. The water may be eliminated by the alcohol plan, or by drying, as given in the same chapter.

The pellicle is then dissolved in $2\frac{1}{2}$ ounces of alcohol and $2\frac{1}{2}$ ounces of ether. It will be noticed that the proportion of pyroxylin to silver bromide is too small. Plain collodion made as follows should therefore be judiciously added, till a silver of good quality is obtained:—

| | | |
|--------------------|--------|-----------|
| Pyroxylin ordinary | | 50 grains |
| Ether .720 | | 5 ounces |
| Alcohol .805 | | 5 „ |

This must be added judiciously. It will probably be found that as much as 5 ounces of this will have to be added; but a good deal depends on the quality of the pyroxylin.

The emulsion should be orange when mixed, and also after washing. It should be powdery to the touch when a plate is coated with it. It will be found to be as rapid as a wet plate, and if a preservative be used (see Chap. XLI.) which will stand the employment of undiluted ferrous oxalate, it will be found, if rightly prepared, a good deal more sensitive. The development takes place by the alkaline method if preferred. An emulsion may be made by the same formula as above, omitting the ammonia. It will be found slower.

CHAPTER XXXIX.

COLLODIO-ALBUMEN EMULSION.

THE writer introduced to the photographic public an emulsion made with albumen, which proved to be very sensitive, and some skilled photographers were pleased with it. The process is given here, as it may, perhaps, be used as a starting point from which other emulsions may be satisfactorily deduced. In the hands of the writer the images were inclined to be thin, but when chloride is introduced, it is found that this lack of density vanishes to a great extent, and leaves a very delicate and printable image. The following is the mode of preparation:—16 grains of ordinary cotton are dissolved in 6 drachms of ether (.730) and 4 of alcohol (.805), and the plain collodion thus formed decanted. 20 grains of zinc bromide are dissolved in a small quantity of alcohol, and enough bromine water added to tinge the solution with a very pale yellow. This is added to the above amount of plain collodion. For each half ounce of the above, 1 grain of dried albumen is taken and dissolved in the least possible quantity of water, or 8 drops of the white of an egg may be dropped into a drachm of alcohol, and thoroughly stirred. Either of these solutions is then carefully dropped into the collodion (placed as usual in a jar), and well stirred up. This should form an emulsion of albumen in the collodion. Forty grains of silver nitrate are next added in the way pointed out on page 33, after having

been dissolved in the smallest possible quantity of water and boiling alcohol. A beautifully smooth emulsion should result from this. Mr. Berkeley, who has tried this emulsion, proceeds in a slightly different way ; he adds the cotton to the ether, then adds the albumen, and finally adds the amount of zinc bromide in the necessary amount of alcohol.

The amount of silver nitrate added ensures that there is an excess of at least two grains in each ounce of the emulsion.

Instead of the emulsion being made entirely with zinc bromide, greater density may be obtained by omitting four grains of it, and adding four grains of calcium chloride.

The emulsion is next poured out into a dish, and the ordinary manipulation carried out. After a couple of washings, it may, however, advantageously be covered with a weak solution of silver nitrate, and again washed till the traces of silver are very faint.

The pellicle should be re-dissolved in equal quantities of ether and alcohol, and finally there should be about seven grains of the pyroxyline, as originally used, to each ounce of the mixed solvents.

The emulsion, when finished, generally gives a tender blue by transmitted light, and is seemingly transparent. It may have a tendency to curl off the plate on drying, in which case the addition of a little ordinary washed emulsion will correct it. It will develop with plain pyrogallie acid, and can be intensified by pyrogallie and citric acid, with the addition of a few drops of silver nitrate solution ; or it can be developed by the alkaline developer, or the ferrous oxalate developer, or the hydrosulphite developer. Some photographers have found a tendency in it to form blisters when developing. This has not happened to the writer when the developer was kept above 60° F. In some hands this emulsion is extremely rapid—so much so, as to require very considerably less exposure than an ordinary wet plate.

CHAPTER XL.

PREPARATION OF THE PLATE.

WHEN we require a glass plate to use without a substratum, we usually soak the plates in nitric acid and water, and then wash under the tap, and carefully dry with a cloth; a cream of tripoli powder in alcohol is then rubbed over the plate and allowed to dry. When a plate is required for use, the tripoli is rubbed off with a soft cloth, and it is left unpolished; a small piece of blotting-paper is then folded up in the shape of a small spill, and dipped in a solution of albumen in water (the strength is immaterial), and the plate is given an edging by placing the moistened end of the spill beneath the thumb of the right hand, and drawing it round the edge of the plate. By this means a "safe edge" is given to it. The amount of fluid required is so small that the first edge may be dry before the last is finished, and yet sufficient for the purpose will be on the plate.

Some persons rub French chalk or talc over the surface of the plate, and this will be found effective when using washed emulsion, without giving an edging; but we honestly confess that where a preservative is used, this is hardly sufficient. In our own experience a film will adhere to the surface when it is only *once* wetted with

water, but not twice. In this case a substratum must be employed to cause the necessary adhesion of the film to the plate. The following answers:—

| | | | | |
|-----------------|-----|-----|---------------|--------|
| Sheet gelatine | ... | ... | 75 | grains |
| Distilled water | ... | ... | 60 | ounces |
| Ammonia | ... | ... | $\frac{1}{4}$ | ounce |
| Alcohol | ... | ... | 1 | „ |

The gelatine should be first softened in half the quantity of water, and the remainder added in the boiling state, which will dissolve it; when cool the ammonia and alcohol should be added, and it should be carefully filtered.

The substratum introduced by the late Mr. C. Hooper may also be employed.

Albumen may also be used.

| | | | | | |
|--------------|-----|-----|-----|-----|--------|
| White of egg | ... | ... | ... | 1 | ounce |
| Water | ... | ... | ... | 100 | ounces |
| Ammonia | ... | ... | ... | 5 | drops |

50 grains of dried albumen may be substituted for the white of egg. The albumen and water should be well shaken together in a bottle for five minutes, and then be filtered through fine filter-paper, taking care to avoid air-bubbles.

A better formula, however, seems to be one due to Mr. Ackland, and is thus described by Mr. W. Brooks:—

The whites of fresh eggs are collected, and to every 8 ounces, one ounce of water and 24 drops of glacial acetic acid are added, by pouring it into the albumen in a fine stream, and stirring evenly with a glass rod for one or two minutes. The albumen should on no account be beaten or whisked up, or the resulting preparation will be milky. It is allowed to rest one hour or more, and is then strained through coarse muslin or cheese cloth. To the strained albumen is added one drachm of the strongest liquid ammonia (880), when it can be put away in corked bottles and kept for use.

To make a substratum, Mr. Brooks takes—

| | | |
|------------------------|--------|---------|
| Prepared stock albumen | ... | 1 ounce |
| Water | | 1 pint |

This is applied as above. For Dr. Vogel's substratum, see page 115.

The cleaning of the plate is of much greater importance when a substratum is used, than where it is omitted, the great difficulty being to get an even film on the surface; it is impossible to get this if there be the least repellent action between it and water. What the writer recommends is, that the plates be soaked in nitric acid, and be well rubbed with it by means of a pad of cotton wool (*freed from all resinous matter by previous soaking in a strong alkaline carbonate, and then thoroughly washed and dried*), and when the acid is washed away under the tap, that it be followed by a solution of potash 20 grains, alcohol $\frac{1}{2}$ ounce, and water $\frac{1}{2}$ ounce, also rubbed in with a pad of wool. When water flows evenly over the surface, the plate should be rinsed in distilled water, and, after a short draining, the gelatine (except Dr. Vogel's, see above) or albumen solution should be flowed over

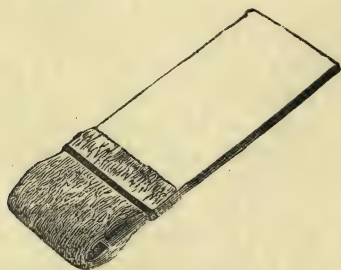


Fig. 28.

it, and drained off immediately. A very thin substratum will thus be given, which will dry rapidly, and be adherent to every part of the surface. Another plan is to use the Blanchard brush. A brush is made of swan's-

down calico, as follows:—A strip of glass, about six inches long by two broad, should be procured, and round one end should be attached, by thread or india-rubber band, a double fold of swan's-down calico. This brush should be dipped in the albumen, and the excess squeezed out against the beaker. The plate, which should be dry, should then be brushed smoothly down the surface in parallel lines to within one-eighth of an inch of its edges, set up to dry on blotting-paper, and protected from dust. When dried (which should be done spontaneously), the plate will be ready for the collodion. We have also found that a squeegee covered over with swans'-down calico, and damp with the substratum, is effective.

Some photographers recommend the use of india-rubber for the substratum.

| | | | | |
|--------------|-----|-----|-----|---------|
| India-rubber | ... | ... | ... | 1 grain |
| Chloroform | ... | ... | ... | 1 ounce |

Or,

| | | | | |
|--------------|-----|-----|-----|---------|
| India-rubber | ... | ... | ... | 1 grain |
| Benzole ... | ... | ... | ... | 1 ounce |

These are flowed over the plate like collodion, the plate, of course, being dry. Unless the solutions be very clear, and free from all residue, a negative taken on a plate so coated is apt to show markings. There are, however, some emulsions which seem to be totally independent of the character of a substratum, and will not show these markings, even when the india-rubber solution is not bright.

Coating the Plate.—When plates are to be coated, the emulsion should be well shaken for three or four minutes, and be then allowed to subside for ten minutes. The top portion should then be filtered through washed cotton wool.* The cotton wool should be placed in the neck of a funnel, and not be too tightly pressed down; and a

* Boiled in soda, and then thoroughly washed.

little strong alcohol passed through it to moisten it. The first lot of emulsion passing through the funnel should be returned to the bottle, and filtered again. The amount of emulsion required varies with the number and size of the plates used. A trial plate is first coated to see if the emulsion flows readily. If it appears to "drag" over the surface, it should be diluted with a little ether and alcohol (2 parts of the former to 1 of the latter). It will be found that in coating a large plate the emulsion should be thinner than for a small plate. When it appears satisfactory, the emulsion should once more be passed through the filter. Coating the plates is next taken in hand. The filtered emulsion is poured over the plate in the usual manner, and the plate tilted up, and rocked to and fro till the ridges and furrows, so often visible in these plates, have disappeared. The surplus collodion should be returned through the filter into another bottle, as by so doing a fresh portion of the emulsion is used for each plate coated, and there will be a consequent freedom from specks due to any dust which may have fallen on a plate previously coated. If this be a washed emulsion, it should now be dried or treated with a preservative (see Chap. XLI.) If it is to be dried, there is nothing so convenient as a hot air bath, such as used by chemists in their laboratory. They can be obtained up to a size which will take $8\frac{1}{2}$ by $6\frac{1}{2}$ plates. It is a good precaution to line the inside with varnished paper, to prevent the remote chance of any metallic specks depositing on the plate during drying. If this be not at hand, the small piece of apparatus recommended by Woodbury is very effective. It consists of an iron tripod stand, such as used in the laboratories, a flat sheet of cast iron, and a spirit lamp when gas is not available. The iron plate is placed on the iron tripod, and the spirit lamp beneath it. It is advisable to place a couple of pieces of blotting-paper beneath the plate which is to be dried. By using the blotting-paper the plate will be dried and heated uni-

formly throughout, which is not the case when it is placed directly on the cast-iron plate, for curvature in either will prevent the two surfaces coming in contact. The heat should be so great that to touch the surface of the blotting-paper is unpleasant to the fingers, and the glass should be allowed to assume the same temperature. It may be laid down as a maxim that the more rapid the drying, the greater freedom there will be from all spots.

Where a preservative is to be employed with a *washed emulsion*, the plate must be washed with water till all greasiness disappears, when it may be applied at once. If an *unwashed* emulsion be used, the plate must be well washed in distilled water, till all excess of haloid salt, if that be in excess—or, *as a rule*, of the silver nitrate, if that be in excess—be thoroughly eliminated. The preservative may then be applied by flooding the film with it, or by immersing the plate in a flat dish or dipping bath containing it. When a plate is flooded with the preservative, sufficient solution should be poured into a measure to well cover the plate. It should then be poured evenly over the film, and drained. A second portion of the preservative should be applied, and worked over the plate for a minute. After this it should be poured off, and the plates set up to dry. The plates are in this case allowed to dry spontaneously, but they are generally improved by a final dry over the iron plate as directed above. If the plates are dried in one of the drying cupboards described in Chap. IV., they will be found to be free from markings, and of better quality than if dried in an ordinary cupboard.

In Chapter XLI. will be found a description of preservatives which may be applied to washed emulsion with success.

As a result of very numerous experiments, the writer has unwillingly come to the conclusion that a washed emulsion without a preservative of some kind is a danger-

ous process in which to place absolute trust. Films which at first would give perfect negatives, will very often show, when kept, spots which refuse to develop. An interesting experiment is to take a plate freshly prepared, and expose half of it to sunlight to darken it, and after the lapse of a fortnight, to expose the other half. Though the first part may show a perfectly uniform darkening of the surface, the other half will, in all probability, show the spots by their refusal to darken. A plate used with a preservative, on the other hand, will blacken equally after any length of keeping. The cause of these spots is rather obscure, but we think we have traced them to a quite unsuspected cause, which, if it prove correct, will indicate another use of the preservative. It must be remembered that the ordinary washed emulsion will be free from the objection if the plates are prepared one day, and exposed and developed within three or four days. This lapse of time is often sufficient for the amateur.

Backing the Plate.—With some kinds of emulsion, more particularly if a gum or albumen preservative be used, the films are very translucent, and the image is subject to the well-known blurring due to light scattered by the silver compound, and reflected from the back of the plate. This defect is in a measure cured by applying some non-actinic varnish to the back of the plate. This backing may be made as follows:—

| | | |
|--------------------------|-----|-----------|
| Powdered burnt sienna... | ... | 1 ounce |
| Gum | ... | 1 " |
| Glycerine | ... | 2 drachms |
| Water | ... | 10 ounces |

The solution can be brushed on with a hog's bristle brush. Ordinary printers' paper coated with gum-arabic, stained with aurine or a blue absorbent dye, and fastened on a plate, is as clean a method of backing a plate as can be desired. Whichever backing is employed, it

should be removed previous to the development of the plate, and it is often convenient to do so after the alcohol has been applied to the surface of the film, and before washing with water. The alcohol repels any water containing the soluble part of the backing, and thus prevents staining of the image. A small tuft of cotton-wool will remove the backing given above.

CHAPTER XLI.

PRESERVATIVES USED WITH EMULSIONS.

ANY emulsion, washed or unwashed, may be used with a preservative, which ensures the plates being uniformly sensitive, and also the absence of those troublesome spots which refuse to develop. Colonel Wortley says that the thorough washing of the film prevents the formation of these spots ; and Mr. Woodbury never finds them when he dries his plates rapidly and at a fairly high temperature. The emulsion used by Woodbury, however, contained resin, and it may be due to this cause that he found the absence of these enemies to emulsion work.

Beer Preservative.—The simplest preservative with which we are acquainted is—

| | | | | | |
|-----------------|-----|-----|-----|-----|---------|
| Beer | ... | ... | ... | ... | 1 ounce |
| Pyrogallic acid | ... | ... | ... | ... | 1 grain |

After the plate is coated, it is washed till all greasiness disappears, and the above is flowed on the film, and allowed to remain on it for a minute. The beer solution may then be drained off, and the plate again washed, or the final washing may be omitted, and the plate be allowed to dry spontaneously. If, after the preservative has been applied, the plate has to be washed, it should be given a final rinse of distilled water.

Mr. England recommends, *after* the plate with the beer preservative has been dried, that it should be washed and given a final flooding with a pyrogallic acid solution, one or two grains to the ounce of water. This procedure, he says, immensely increases the rapidity; it is rather more trouble than the methods already given.

If the beer be left on the plate, and if the dimensions of the latter be more than about five by seven, a substratum (Chap. XVI.) should be used, as the films may have a tendency to blister. It will be found, however, if, *after exposure*, the plate be washed and be allowed to dry, and then be treated with alcohol and water, and be developed, that the film will adhere tenaciously to the plate, and that no substratum will be requisite.

Mr. William Brooks, in the PHOTOGRAPHIC NEWS, described a modified method of applying the beer preservative to washed emulsion plates.

The plate is coated in the usual manner, and when properly set, it is, *without washing*, plunged into a bath made as follows:—

| | | | | |
|-----------------|-----|-----|-----|---------|
| Bitter ale... | ... | ... | ... | 1 ounce |
| Pyrogallic acid | ... | ... | ... | 1 grain |

Sufficient of this is used to fill a dish to a depth of half-an-inch. The ale should not be of the kind known as sweet or mild, as both these contain too much saccharine matter. The plate is left in the preservative till there is no repellent action due to the ether and alcohol. It is then taken out and dried spontaneously, a final warming, previous to storing, being given to it by means of a drying oven or a hot water tin. The plates do not require backing unless the emulsion be thin. The exposure necessary must be ascertained by a trial plate.

Mr. Brooks states that he has kept plates prepared by this formula five months before exposure, and about the same time between exposure and development, and has developed them without stain or speck.

The following preservatives may also be used with the emulsion plates.

Carey Lea's Preservative.—Mr. Carey Lea's "Litmus Preservative" and tannin preservatives are as follow:—

"Cover a quarter of a pound of good litmus with hot water; set a basin or plate over the bowl, and put in a warm place for a day; throw the paste upon a filter, and pour on hot water till the filtrate amounts to a quart (the filtration is slow); add a drachm of carbolic acid, and the litmus solution keeps good indefinitely.

| | | | |
|-----------------------------------|-----|-----|-----------|
| Litmus solution... | ... | ... | 1 ounce |
| Water ... | ... | ... | 6 ounces |
| Gum-arabic ... | ... | ... | 90 grains |
| Sugar (fine white) ... | ... | ... | 90 " |
| Acetic acid (No. 8, or Beaufoy's) | | | 25 minims |

"The above quantity makes a convenient bath for a $6\frac{1}{2}$ by $8\frac{1}{2}$ plate.

"Throw the collodio-bromized plate into a pan of water until the greasy marks are gone, and then pass it into this bath, where it should remain, with occasional agitation, about ten minutes. The time is not important; five minutes will be sufficient: fifteen will do no harm."

The tannin preservative is as follows:—

| | | | | |
|----------------|-----|-----|-----|-----------------------|
| Water ... | ... | ... | ... | $7\frac{1}{2}$ ounces |
| Gum arabic ... | ... | ... | ... | 90 grains |
| Sugar ... | ... | ... | ... | 90 " |
| Tannin ... | ... | ... | ... | 15 " |

The washing of the plate is the same as above.

Regarding these two preservatives, Mr. Lea says: the litmus gives the softest and most sensitive plates, but needs an intenser cotton. The latter of the two preservatives will work well with a wider range of pyroxylin than the former, and give a brighter picture. The tannin is the easiest to succeed with, but the litmus, when well managed, undoubtedly gives the best negatives. In

either case, the negatives are very beautiful; better looking or better printing negatives cannot be got with the wet process. The development may proceed by the strong alkaline development (page 261), or by the process as described by Mr. Cooper (page 237).

The Coffee Preservative.—A coffee preservative is made as follows:—

- | | | | |
|---------------------------------|-----|-----|-----------------------|
| 1.—Best coffee ... | ... | ... | $\frac{1}{2}$ ounce |
| White sugar ... | ... | ... | 90 grains |
| Boiling distilled or rain water | | | $5\frac{1}{2}$ ounces |
| 2.—Gum-arabic ... | ... | ... | 90 grains |
| Sugar candy ... | ... | ... | 20 " |
| Distilled water ... | ... | ... | $5\frac{1}{2}$ ounces |

When No. 1 is cooled, both solutions are filtered, and the preservative applied by floating or by immersing the washed plate in a flat dish containing the solution.

The plate will require a substratum unless the precaution indicated above be observed.

Tannin Preservative.—A simple preservative is made with tannin as under:—

- | | | | |
|--------------------|-----|-----|-----------|
| Tannin (pure) ... | ... | ... | 15 grains |
| Distilled water... | ... | ... | 1 ounce |

The plate is washed, and the preservative applied as above.

Albumen Beer Preservative.—The following are prepared:—

- | | | | |
|------------------------------------|-----|-----|----------------------|
| 1.—Dried albumen (or white of egg, | | | |
| prepared as at page 79, 1 oz.)... | | | 25 grains |
| Water ... | ... | ... | 1 ounce |
| Liquor ammonia ... | ... | ... | $\frac{1}{2}$ drachm |
| 2.—Ordinary bitter beer ... | ... | ... | 1 ounce |
| 3.—Ordinary bitter beer ... | ... | ... | 1 " |
| Pyrogallic acid ... | ... | ... | 1 grain |

The plate, after washing, is flowed over with equal

parts of 1 and 2, which are allowed to be in contact with the film for one minute. It is then thoroughly washed, and flowed over with No. 3, and set up to dry.

These plates are developed by any of the alkaline developers given in the next chapter. Reducing the amount of pyrogallic acid given to one-third will cause a thin negative, which can be readily intensified by the ordinary intensifier. This preservative gives great beauty and delicacy to the negative, and subsequent intensification is better than getting density by the alkaline developer alone. The plates prepared with the albumen solution are exceedingly rapid and safe.

A substratum is required for large plates.

Col. Wortley's Preservative is as follows, and he recommends it as giving freedom from blisters often found with gum preservatives.

The following stock solutions are prepared :—

No. 1.—Salicine, enough to make a saturated solution in distilled water.

No. 2.—Tannin 60 grains
Distilled water 1 ounce

No. 3.—Gallic acid... ... 48 grains
Alcohol 1 ounce

To make the preservative, take of—

| | | | | |
|--------|-----|-----|-----|-----------------|
| No. 1. | ... | ... | ... | 2 ounces |
| No. 2. | ... | ... | ... | 1 ounce |
| No. 3. | ... | ... | ... | $\frac{1}{2}$ " |
| Sugar | ... | ... | ... | 40 grains |
| Water | ... | ... | ... | 7 ounces |

This preservative may be used over and over again with occasional filtering. The plates are best immersed in it.

Red Gum Preservative.—The following alcoholic preservative may be found useful:—Australian red gum, a saturated solution, in equal parts of alcohol and water.

The plate is washed, flooded with equal parts of alcohol and water, and, after the preservative is floated on, it is dried spontaneously. The gum must be removed by alcohol and water, and the development will take place in the ordinary way. No substratum may be required.

Gum Guaiacum Preservative.—This preservative is really mixed with the emulsion itself. It is prepared by making a saturated solution of gum guaiacum in alcohol .805. One part of this to from 20 to 25 parts of the washed emulsion are mixed, and the plate coated in the usual manner. It is allowed to dry at a temperature of about 100° F., or else spontaneously. This is an excellent addition to make to a horny collodion.

The writer has tried the above preservatives, and has therefore given them to the reader; but there is no doubt that almost any of the well-known preservatives might have been applied with equal success.

CHAPTER XLII.

DEVELOPMENT OF THE PLATE.

For emulsion work, an alkaline (or kindred) developer of some kind is almost an essential, for though faint detail can be developed by pyrogallic acid alone in *most* cases, such a procedure entails a prolonged exposure.

The following are formulæ for the alkaline developer which the writer can recommend, having been in use by him for several years past :—

- | | | | |
|------------------------|-----|-----|-----------|
| (1).—Pyrogallic acid | ... | ... | 6 grains |
| Water | ... | ... | 1 ounce |
| (2).—Potassium bromide | ... | ... | 20 grains |
| Water | ... | ... | 1 ounce |
| (3).—Ammonia | ... | ... | 1 part |
| Water | ... | ... | 32 parts |

To develop, 2 parts by measure of (1), 2 parts of (2), and 1 part of (3) are taken and well mixed in the developing cup. If an albumen or gum preservative be used, No. 2 may be reduced to 1 part.

The developer given by Col. Wortley is as follows :—

- | | | | |
|----------------------|-----|-----|-----------|
| (a).—Pyrogallic acid | ... | ... | 96 grains |
| Methylated alcohol | ... | ... | 1 ounce |

(b).—Potassium bromide ... 120 grains
 Water distilled ... 1 ounce

(c).—Ammonium carbonate ... 80 grains
 Water ... 1 ounce

Or,

(c).—Liquor ammonia 880 ... 6 minims
 Water ... 1 ounce

By the last formula, 6 minims of (a), 3 minims of (b), and three drachms of (c) are taken and mixed.

M. Chardon's developer is as follows:—

1.—Ammonium carbonate ... 10 grains
 Potassium bromide ... 2 „
 Water... ... 1 ounce

(Care must be taken that the carbonate is pure.)

2.—Pyrogallie acid ... 50 grains
 Alcohol ... 1 ounce

To develop, the following proportions are taken:—

No. 1 ... 1 ounce
 No. 2 ... 10 to 15 minims

The image will appear very rapidly if the emulsion has been properly prepared.

We will now imagine that the plate has been exposed, and that we are to develop the image. After taking the plate out of the slide it is carefully dusted, and, if necessary, a solution of equal parts of alcohol and water is flowed over it to soften the film. It is then either washed under the tap, if the water supply be of good quality, or is immersed in a dish of rain-water previously filtered through charcoal. When all repellent action between the spirit and water is obliterated, the mixed proportions or solutions indicated above are carefully flowed over the plate, and almost immediately poured back. The image ought to appear gradually and without veil. If it shows

unwillingness to appear, a fresh solution should be made, omitting half the bromide, and this will probably be effected.

To develop a plate having a preservative, a little thought should be taken as to the nature of the latter, as has been indicated in the last paragraph. It is evidently useless to waste alcohol if it is not soluble in it. In cases where it is insoluble, the preliminary flooding with the spirit should be omitted, and the soluble matter entirely removed by water. Since the object of the alcohol was to open the pores of the collodion, evidently the same will be accomplished by removing the soluble matter which filled them up.

Should there not be sufficient density, resort must be had to the ordinary acid intensifier.

| | | | |
|--------------------|-----|-----|----------|
| 1.—Pyrogallic acid | ... | ... | 2 grains |
| Citric acid | ... | ... | 2 " |
| Water | ... | ... | 1 ounce |

And,

| | | | |
|-------------------|-----|-----|-----------|
| 2.—Silver nitrate | ... | ... | 20 grains |
| Water | ... | ... | 1 ounce |

The plate must be well washed before using this. Sufficient of No. 1 to cover this plate should be flowed over it, and 4 or 5 drops of No. 2 dropped into the cup, and the solution from off the plate returned on to it. The intensification should then proceed till sufficient density is secured.

The developer which Mr. Brooks recommended for his process is as follows. It is an excellent formula, and, as he gives some valuable hints about conducting development, which apply to all processes alike, we give his remarks *in extenso* :—

“After the plate has been exposed, take it on a pneumatic holder, and flow over it equal parts of alcohol and water. I must here add a caution not to use the alcohol

too strong, or it will attack the film unevenly, and cause mottling, especially in the high-lights, as I am sure, from past experience, this is one of the causes. It is not seen so much in the half-tone, and scarcely at all in masses of foliage, or where the subject is well broken up. If mottling does occur, it is most at the thick end of the plate. I do not know if this corresponds with the experience of other workers. If the alcohol is used without diluting (say of s. g. of .825) the mottled markings are very large, and as the alcohol is diluted with water, they become smaller and smaller till they disappear altogether. I generally allow it to soak well into the film for about two minutes, of the strength mentioned above (half water and half alcohol). Methyated spirit answers every purpose, providing that it is free from gum (if contaminated with gum it turns milky on the addition of water). If a quantity of plates are to be developed, I prefer to immerse each plate in a tray containing the spirit, as it is then done effectually. The plate is then taken and allowed to soak in a dish of clean water, and rocked about until the water flows evenly over the surface. Previous to applying the developer, flood the plate with the following:—

| | | |
|-------------------------|--------|---------|
| Stock albumen (page 79) | ... | 1 part |
| Water | | 4 parts |

Allow this to soak well into the film; well rock the plate to ensure even action; not less than one minute must be allowed for this part of the operation. The plate is then slightly drained, and the alkaline developer applied, made from the following stock solutions:—

| | | |
|---------------------------------|-----|-----------|
| P.—Pyrogallic acid (best) | ... | 96 grains |
| Absolute alcohol | ... | 1 ounce |
| A.—Sat. sol. ammonium carbonate | ... | 4 ounces |
| Potassium bromide | ... | 2 drachms |
| Water | ... | 8 ounces |

A few drops of solution P for 9 by 8 plates (say 5 drops);

and 1 ounce of solution A are mixed in a perfectly clean measure, and at once poured over the plate; as soon as it is covered it must be rocked vigorously for a few seconds, so as to make it blend with the albumen on the plate; and if the plate has been properly exposed the image will at once make its appearance, gradually acquiring intensity.

"After the developer has been on for some little time, should it apparently cease in its action, drain it off, and again apply a little of the prepared albumen solution for about half a minute; drain again, and apply the alkaline developer as before; the image will then, perhaps, rush out very rapidly. This method can be repeated as often as necessary; but, as a rule, with a properly exposed plate, one application of the albumen is sufficient. If more density is required, a drop or two more of P solution can be added. If too much pyrogallic is used, a very hard negative is the result, so it must be used with judgment. I have actually developed a 24 by 18 plate to full printing density with only half a grain of pyrogallic. The formula given for solution A is given for work under normal conditions. In the winter time the bromide can be reduced one-half, and in very warm weather it can be increased.

"I have used the albumen as given above for several years, and the more I use it the more I like it, as it gives an image so much like a good wet plate taken under the best conditions.

"Should it be desirable, the intensity can be brought up in the ordinary way before fixing with acid pyrogallic and silver, same as for wet plates (see page 157.) The plate must be well washed to free it from all traces of ammonia, and before the silver is added to the acid pyrogallic it is first applied to the plate alone, which will generally be sufficient to neutralize whatever may have remained in the pores of the film."

Some prefer to develop their plates in a dish: indeed, for ease of manipulation, a dish is highly desirable. Care

must be taken in this case that sufficient solution be taken fully to cover the plates; for an $8\frac{1}{2}$ by $6\frac{1}{2}$ plate, and an ordinary 10 by 8 porcelain dish, 4 ounces will be required.

The next developer, and which, for this process and also the gelatino-bromide process, should become a general favourite, is the ferrous oxalate developer.

The modes of preparing the ferrous oxalate solution will be found in Chapter XXIII. Our mode of procedure with the developer is as follows:—If the saturated solution of the developer (made by dissolving ferrous oxalate in a saturated solution of potassium oxalate) be used, we dilute it with half its bulk of water, and add to every ounce 1 drachm of a solution of potassium bromide in water (20 grains to 1 ounce), and apply this to the film after washing, as described above. If the image appears slowly, we add half the original quantity of the ferrous oxalate undiluted, and then, if the exposure be anywhere near correct, this will bring up the requisite density. Should more density be required, we intensify as given at page 93.

Should the image refuse to come out even with the stronger developer, one drop of a $\frac{1}{10}$ th per cent. solution of sodium hyposulphite to each ounce of developer will have an accelerating effect (see page 152).

The exposure required for this developer seems to be about two-thirds of that required for the alkaline developer given above, and is, therefore, a decided gain to the photographer.

There is a great charm in this developer, the plates gaining intensity steadily, and without any tendency of being overdone, and the negatives give brilliant prints.

The ferrous-citro oxalate developer (see page 165) is also applicable for development. It works rather slower, but can be used without the addition of *any bromide*. The sodium hyposulphite may be used with it as with the ferrous oxalate developer.

A negative that is fully developed should show reduced silver bromide next to the glass plate in the most opaque parts; so complete should this be, that if the image be dissolved away by nitric acid, we should have a positive picture left behind formed of unalterable bromide, having perfect gradation.

In the early days of emulsion making a weaker developer was made use of, and as for some plates it is still useful, we insert it here for the guidance of students.

| | | | |
|------------------------|-----|-----|----------|
| No. 1.—Pyrogallie acid | ... | ... | 3 grains |
| Water... | ... | ... | 1 ounce |

(This will not keep long, but should be made when required.)

| | | |
|---------------------------|-----|------------|
| No. 1.—Ammonium carbonate | ... | 1½ drachms |
| Water | ... | 1 ounce |

Or,

| | | |
|-----------------------|-----|----------|
| No. 2.—Liquor ammonia | ... | 1 part |
| Water | ... | 12 parts |

| | | |
|--------------------------|-----|---------|
| No. 3.—Potassium bromide | ... | 1 grain |
| Water | ... | 1 ounce |

| | | |
|-----------------------|-----|-----------|
| No. 4.—Silver nitrate | ... | 20 grains |
| Citric acid | ... | 25 „ |
| Water | ... | 1 ounce |

Nos. 2, 3, and 4 will keep infinitely.

The film should then be well washed under the tap. If there be every reason to suppose that proper exposure has been given, make a developing mixture in the following proportion:—

| | | |
|-------|-----|----------|
| No. 1 | ... | 1 drachm |
| No. 2 | ... | 1 drop |
| No. 3 | ... | „ |

Sufficient should be taken to well cover the plate. Nos.

2 and 3 should be first dropped into the developing cup, and finally No. 1 is added. (The necessity of stirring is prevented by this procedure.) Flood this over the plate. The image, if everything be *en regle*, should appear quickly, and the developer should be worked over the plate till all detail appears by reflected light. When this happens, another drop of No. 2 to each drachm should be dropped into the measure, and the solution poured back on to it as before, and the intensification with the stronger ammoniacal solution proceeded with. The intensity will gradually be increased, and it may happen that the requisite density will be obtained. Should the density not be sufficient, one drop of No. 4, with a drachm of No. 1, may be mixed, and intensification takes place in the ordinary manner. In the writer's experience, the colour and printing qualities of all negatives by this process are improved by even a slight application of the intensifier.

Should the negative flash out at once on the application of the first developer, it is a sign of over-exposure of the plate. The developer should immediately be returned to the cup, and the plate washed. Two drops extra of No. 3 must be added to the developer, and the development proceeded with as before. The potassium bromide keeps the shadows bright, and acts as a retarder; so much has it the latter qualification, that if a large quantity be added, the plate will refuse to develop at all. It is better to fix an over-exposed picture immediately the detail is all out, and intensify with pyrogallie acid and silver afterwards.

If traces of the picture refuse to appear in three or four seconds after an application of the primary developer, a fresh developer should be made up similar to the above, *omitting* the bromide of potassium. If the picture refuse to appear satisfactorily when this course is adopted, the plate is hopelessly under-exposed. When the detail is well out, the intensification should be carried on as given at page 263.

Fixing Solution.—The negative should be fixed with potassium cyanide or sodium hyposulphite.

| | | | |
|-------------------|-----|-----|-----------|
| Potassium cyanide | ... | ... | 25 grains |
| Water | ... | ... | 1 ounce |

Or,

| | | | |
|---------------------|-----|-----|----------|
| Sodium hyposulphite | ... | ... | 1 ounce |
| Water | ... | ... | 6 ounces |

The first may be flowed over the plate, but a dipping bath for the latter will be found advantageous for studio work. There are some images which will not stand the cyanide, and in rare instances some will not stand prolonged immersion in the hyposulphite; it may be because the metallic silver is in a very fine state of division. This seems all the more probable since we know that in this state it is attacked by the cyanide. When all the bromide is dissolved from out of the film, the plate should be well washed back and front. It is not amiss to give a dip in a solution of alum, as used for gelatine plates, if hyposulphite has been used, since it effectually decomposes it.

The plate should be allowed to dry spontaneously, away from dust, and it should then be varnished. Varnish such as is used for wet plates should be procured and applied, as given at page 161.

CHAPTER XLIII.

COLLODIO-CHLORIDE EMULSION FOR DEVELOPMENT.

IN the previous processes it will be seen that silver bromide forms the staple sensitive salt, though both iodide and chloride have been introduced into the emulsion, but in small quantities. The use of chloride by itself has, till quite recently, been inadmissible, on account of the difficulty of producing a chemical developer suitable for it. Dr. Eder and Captain Pizzighelli found that for gelatino-chloride plates, ferrous citrate in a weak form gave good development. The developer was very weak, however, in the form they gave, and the writer introduced the ferrous-citro-oxalate form, which has proved suitable for collodio-chloride plates.

There are two formulæ for collodio-chloride emulsions, one with excess of silver, and the other with an excess of chloride. For most purposes the latter is the one we prefer, since it can be made and used in a quarter of an hour when required. What is usually called collodio-chloride is totally unfit for chemical development, and it is misleading to class it under this denomination, since it has a large proportion of citrate in its composition. To make the collodio-chloride we proceed as follows :—

Weigh out the following—

| | | |
|--------------------------------------|-----|-----------|
| Pyroxyline (any easily soluble sort) | ... | 10 grains |
| " | ... | 5 " |
| Calcium chloride ... | ... | 20 " |
| Silver nitrate ... | ... | 50 " |

Dissolve the calcium chloride in $\frac{1}{2}$ ounce of alcohol .805, by warming over a spirit lamp. Place the 5 grains of pyroxyline in 2-ounce bottle, and pour on it the alcohol containing the calcium. After a couple of minutes add $\frac{1}{2}$ ounce of ether, when the cotton will dissolve.

Dissolve the 50 grains of silver nitrate in a test-tube in the smallest quantity of water, and add to it 1 ounce of boiling alcohol .805, and mix. Previous to this the 10 grains of pyroxyline should have been placed in a four-ounce bottle, and the alcohol containing the silver should be poured on. Next add 1 ounce of ether, little by little, with continuous shaking. The silver nitrate may very probably partially crystallize out, but that is of very little consequence. Take the two bottles into the dark-room (a room glazed for wet-plate work will answer perfectly), and *pour gradually the calcium chloride collodion into the silver nitrate collodion*—on no account *vice versa*. The resulting emulsion, of course, is silver chloride in an extremely fine state of division. A plate coated with it should show a canary colour by transmitted skylight, and a thickish film should make a gas flame appear ruby-coloured. The emulsion may be washed in the usual way, if required (see page 51); but, when washed, and used simply dried after washing, it is, like other collodion emulsion prepared with an excess of haloid, rather insensitive. Before doing anything with the emulsion, however, a plate should be coated, washed under a tap, and placed in the dark slide. The slide should be taken into white light, and half the front pulled up for a second, and then closed. Ferrous-citro-oxalate developer, as given at page 165, should then be applied, and the result noted. A blackening of

the film may ensue. If correct on the application of the developer, the film should not show any reduction of the chloride, except on the exposed half of the plate. Should blackening take place, nitric acid may be added; but that rather rots the film if kept too long in contact with the emulsion, which would be the case if it is to remain unwashed. A simpler plan is to add a soluble chloride which would form a double chloride. Three or four drops of a 20-grain solution of cupric chloride (chloride of copper) in alcohol should be added to the emulsion, and shaken up, and immediately the fog disappears. Two or three drops of gold tri-chloride, or of cobaltic chloride of a similar strength as the copper chloride, would answer equally as well.

So far as regards the making of the emulsion. The next point is the preparation of the plates. As was said before, it can be washed, but we really see no advantage in so doing. Polished and edged plates (see page 77) may be coated, washed, and then simply flooded once over with—

| | | | | | |
|-----------------|-----|-----------------------|-----|-----|----------|
| Beer | ... | ... | ... | ... | 5 ounces |
| Sugar (white) | ... | 1 moderate sized lump | | | |
| Pyrogallic acid | ... | ... | ... | ... | 5 grains |

These, when dry, will be very sensitive, and put to shame many a collodio-bromide emulsion. Any of the preservatives given in Chap. XLI. may also be used. To develop, rinse, and then simply immerse them in a dish containing the ferrous-citro-oxalate. In a short time the image will begin to appear, and gradually gain strength. The colour of the image is a beautiful ivory black, and admirably suited for collodion transfers. If a warmer tint is required, tone in a dish with—

| | | | | |
|---------------------------|-----|-----|-----|-----------|
| Uranium nitrate | ... | ... | ... | 10 grains |
| Ferricyanide of potassium | ... | ... | ... | 10 " |
| Water | ... | ... | ... | 10 ounces |

The colour will rapidly warm, and would eventually become a pretty chocolate colour.

It will be noted that an emulsion prepared in this way may be developed by the ferrous-citro-oxalate *without any restrainer*.

They will also develop with:—

| | | | | |
|-------------|-----|-----|-----|-----------|
| Hydrokinone | ... | ... | ... | 10 grains |
| Water | ... | ... | ... | 1 ounce |

to every ounce of which are added 3 or 4 drops of a saturated solution of carbonate of ammonia.

The emulsion may also be made with an excess of silver nitrate, in which case, in the above formulæ, seventy grains of silver nitrate should be used. Fog may be prevented by adding 2 or 3 drops of strong nitric acid to the calcium chloride collodion, or it may be eliminated by the use of bichromate of potash, or by hydrochloric acid, or by cupric, cobaltic, or auric (gold) chlorides, after the excess of silver has been washed away. In fact, the same procedure should be adopted as in the collodio-bromide process. The development of this emulsion is carried on as above.

Collodio-bromo-chloride Emulsion.—A very capital emulsion is formed by mixing $\frac{2}{3}$ part of an unwashed collodio-bromide emulsion with $\frac{1}{3}$ part of an unwashed collodio-chloride emulsion. The same proportion of washed emulsions may also be mixed with advantage. The development of this emulsion is most advantageous when an unrestrained developer such as the above is used.

CHAPTER XLIV.

DEFECTS IN COLLODION EMULSION PLATES.

It is somewhat difficult to name the especial defects found in the emulsion dry plates, but we will endeavour to point out the principal ones.

Blisters in the film.—May be due to a preservative, more particularly if it contain gummy matter. Thus, with the beer, or the gum-gallic or coffee preservatives, these may make their appearance. The remedy has already been given.

Black spots on development are usually due to dust being allowed to settle on the film whilst drying; decomposing organic matter in fine particles is also a fruitful source of these annoyances.

Insensitive patches or spots on development have not yet been tracked to an origin; but if a preservative be employed, they will rarely be met with. They seem to be due to impurities in the pyroxylin, since with certain preparations they are altogether absent.

Crape markings in the film are usually due to the solvents of the emulsion being too aqueous; or they may be due to the emulsion not having been shaken up shortly before being used, or to the bromide being too coarse.

Thin transparent films with washed emulsion are usually due to the last two causes.

The emulsion refusing to flow properly is due to deficiency of solvents. This is frequently met with if the same emulsion be used for coating many plates. It should be diluted down with 1 part of alcohol (.812) to 2 of ether (.720).

When the film tends to peel off the plate, the pyroxylin is probably of too contractile and horny a nature, in which case the proper treatment is, to mix it with an emulsion made with one of a more powdery character, or to mix a little gum guaiacum dissolved in alcohol with it.

Circular insensitive patches in the centre of the plates are sometimes met with in hot weather, when a pneumatic plate-holder is used.

The cause of fog has been pointed out in the first chapter, and need scarcely be alluded to again. To eliminate it in a washed emulsion, the careful addition of a few drops of a dilute solution of iodine in alcohol will prove effective. With such an emulsion, when used with a preservative, a dip in a 10 per cent. solution of hydrochloric acid in water will eliminate all fog. In an unwashed emulsion the addition of nitric acid will effect a cure.

Plates which fog through having been exposed to light may be rendered available for use by washing off any preservative they may have on them, and immersing them in a hock-coloured solution of potassium bichromate, or by water faintly tinged with potassium permanganate, or with a 10 per cent. solution of hydroxyl or hydrochloric acid in water. After washing, a preservative may again be applied.

Plates which fog under development, when the emulsion is not in fault, must owe this defect to one of two causes: 1st, to the light of the developing room; or, 2nd, to the developer. The first cause is easily tracked, as a plate may be prepared and developed in almost absolute darkness without receiving any exposure to ordinary light. If, after a short application of the developer,

no fog is found, the light used during development is in fault. If the plate fogs, the developer is wrong. In this case, try making up fresh solutions, and using more soluble bromide as a restrainer. With the ferrous oxalate developer want of bromide is often the cause of fog.

Drying markings in a film are sometimes met with. They generally form a sort of ripple marking near one edge. They are usually found when impure water is used for the final washing of a plate, and are absent when a final rinsing with distilled water is given. With plain washed emulsion these markings are never met with unless the temperature of the drying oven is high.

Thick specks in a plate are usually due to the dried emulsion from the neck of the bottle mixing with the solution, and finding a resting-place in the film.

CHAPTER XLV.

EMULSION PROCESSES FOR PRINTING.

Collodio-Citro-Chloride.—To prepare a citro-chloride emulsion is not very easy at first sight, since the citrates are very insoluble in alcohol, and it is necessary to have some such body present in the collodion to form an organic compound of silver to give vigour to the image. It is very easy to do, however, by a little artifice which we have thought might be worth describing. Citrate of ammonia is insoluble in alcohol, and therefore rather difficult to introduce into an emulsion in the ordinary manner; but it can readily be introduced into collodion by the following procedure. Take ten grains of pyroxylin, and cover it with half an ounce of alcohol in which 20 grains of citric acid are dissolved, and then add 1 ounce of ether. This forms collodion containing citric acid. In order to get citrate of ammonia into the collodion in a very fine state of emulsion, ammonia (gas) dissolved in alcohol is added to the collodion. This is effected by inserting a bent tube in a cork in a test tube which is a quarter filled with liquor ammonia. Placing this in warm water—in fact, nearly boiling water—the ammonia is given off rapidly, and can be made to pass through alcohol in another test tube. The alcohol absorbs the

ammonia, and takes up a large proportion of gas, as those who use sal-volatile may be aware.

This ammoniacal alcohol is next added to the collodion containing the citric acid, little by little, with shaking and stirring, and sufficient is added till reddened litmus paper shows a very slight trace of alkalinity. A very fine emulsion of citrate of ammonia is thus formed, the grain of which is indistinguishable by the naked eye, and, like other emulsions when first mixed, is orange-coloured when spread upon a glass plate. The emulsion is again rendered slightly acid by the addition of a few drops of a solution of citric acid in alcohol. If an emulsion of citrate of silver be required, there are two ways of effecting it—one by dissolving (say) 10 grains of silver nitrate in the least possible quantity of water, to which is added one drachm of alcohol, and gradually dropping it into the collodion containing the citrate. It sometimes happens that this gives a granular emulsion. If, however, the silver nitrate be coarsely powdered and added to the emulsion, a very fine emulsion of citrate of silver is produced by shaking. This may be washed in the usual way, or may be precipitated by pouring in a fine stream into water. Another method of forming the citrate of silver is to pour out the emulsion of citrate of ammonia into a flat dish, and, when well set, to cover it with a solution of silver nitrate. It is then drained from the silver, washed, and dried as usual. When re-dissolved, the emulsified citrate of silver should be excessively fine.

To prepare a collodio-citro-chloride emulsion, two plans may be adopted: either to dissolve 20 grains of dry calcium chloride in a small amount of alcohol, and add it to the citrate of ammonia emulsion, and then to add 80 grains of silver nitrate to it in the usual way. What we prefer, however, is to make a collodio-chloride emulsion separately, and then to mix the citrate of silver emulsion with it, according to taste.

To make a pure collodio-chloride emulsion, I dissolve 20 grains of calcium chloride in half-ounce of alcohol; add to it 5 grains of pyroxylin, and then $\frac{1}{2}$ ounce of ether. To 1 ounce of plain collodion made similarly, I add 60 grains of silver nitrate dissolved in the smallest quantity of water, to which is added one drachm of warm alcohol. This produces an emulsion of silver nitrate in the collodion. To this the chlorized collodion is added drop by drop, with stirring or with shaking in a bottle, and a perfect emulsion of silver chloride should result. This can be poured out to set in a dish as usual, and washed, dried, and re-dissolved; or can at once be poured out in a fine stream into a large bulk of water, squeezed, soaked in alcohol twice, wringing out in a cloth all excess of alcohol each time. It can then be re-dissolved in the one ounce of ether and one of alcohol, and should give a good emulsion. The two emulsions may then be mixed together as before stated. It is well to dissolve about 5 grains of silver nitrate in water and alcohol, and add to the emulsion in order to increase the rapidity of printing.

Any well-sized paper may be used with this collodion emulsion, but we prefer the enamelled paper, such as is used for collotype printing. The paper is turned up round the edges for about $\frac{1}{8}$ of an inch, to make a shallow tray, and placed on a sheet of glass for steadiness. The collodion emulsion is then poured on to the paper till well covered, and all excess is drained off into the bottle. It is then allowed to dry. It is now ready for printing, which is done to a greater depth than for prints on albumenized paper. After washing it may be toned by the following:—

| | |
|----------------------------------|-----------------------|
| No. 1.—Ammonium sulphocyanate... | 1 $\frac{1}{4}$ ounce |
| Sodium hyposulphite | ... 45 grains |
| Sodium carbonate ... | ... 15 „ |
| Water ... | ... 50 ounces |

| | | | |
|--------------------------|-----|-----|---------------|
| No. 2.—Gold tri-chloride | ... | ... | 30 grains |
| Chalk | ... | ... | 1 teaspoonful |
| Water | ... | ... | 50 ounces |

Equal quantities of these are taken and mixed, and the toning proceeds as usual. The prints ordinarily take from two to ten minutes to tone. If a longer time be required, add more gold till the desired effect is produced. This toning bath can only be used once.

We have also found that a good tone may be given by using the lime bath, or by the baths given at page 195. These prints should be permanent, and possess a rare beauty.

Gelatino-Citro-Chloride.—The writer has introduced a process of printing by means of a citro-chloride in gelatine, which can be applied to paper and glass. The method of preparation is as follows:—

| | | | |
|--------------------|-----|-----|------------|
| 1.—Sodium chloride | ... | ... | 40 grains |
| *Potassium citrate | ... | ... | 40 " |
| Water | ... | ... | 1 ounce |
| 2.—Silver nitrate | ... | ... | 150 grains |
| Water | ... | ... | 1 ounce |
| 3.—Hard gelatine | ... | ... | 160 grains |
| Soft gelatine | ... | ... | 160 " |
| Glycerine | ... | ... | 1 drachm |
| Water | ... | ... | 3½ ounces |

Nos. 3 and 2 are mixed together, and then an emulsion formed by adding No. 1 in the usual way when forming a gelatine emulsion. When set, the emulsion is squeezed through canvas into cold water, and after allowing it to remain in the water for ten minutes or a quarter of an hour, dissolved up, with the addition of about 3 drachms of alcohol and 2 grains of chrome alum dissolved in 2 drachms of water. Plates or paper are then coated with the emulsion, and printing takes place in the usual

* The citrate may be reduced to 20 grains, and the silver nitrate to 120 grains.

manner. At first the emulsion may appear grainy; if, however, it be boiled for ten minutes, the grain disappears, for the silver citrate is soluble in warm water. The rapidity of printing by the boiling is certainly increased. Plates, when coated, are rather transparent, and, *prima facie*, a vigorous print might not be expected from them. The rapidity of printing is very great; it is more than twice as rapid as ordinary albumenized paper. The image prints of a violet tint by reflected light, and of a rich chocolate colour by transmitted light. If fixed without toning, the colour by transmitted and reflected light is that of burnt sienna, and of great vigour and beauty. Prints can be toned by any of the ordinary toning baths. Borax and chloride of gold gives a pleasant tone; the sulpho-cyanide toning bath gives a black, rather approaching an inky tone. Platinum can be used to tone the fixed print, but it has a great reducing action, and there is a tendency for the whites to become yellowed to a slight extent. No doubt endless variations in the organic salts used might be made, but the citrate answers well.

The prints should be well washed. It is believed that they would not fade in the same way that albumen prints are so prone to do, as the organic salt used is a definite compound, and not one which is so complex and uncertain as the albuminate of silver is. The liability to fade is less with the above formula than with one which has an excess of silver present. The potassium citrate is in large excess; hence no silver will attack the gelatine. Of course this emulsion may be applied to opals or glass, or it may be applied to paper as given in Chap. XXVII.

Mr. Ashman says the following gives a good tone:—

The following will be found capable of giving any tone to the transparency or positive by reflected light, ranging between warm brown and purple black:—

| | | | |
|------------------------|-----|-----|----------|
| Ammonium sulphocyanate | ... | ... | 1 drachm |
| Water | ... | ... | 1 pint |
| Gold terchloride | ... | ... | 1 grain |

Upon adding the gold, it is converted into a sulphocyanate, which will be seen to have a red colour. The precipitate, however, dissolves in the excess of sulphocyanate, and is then ready for use.

Washing before toning is dependent on the formulae employed in making the emulsion; in most cases it will be found advisable. Toning action is first seen at the edges, by the colour changing to a yellowish-brown; soon the whole print assumes a sepia tint, then purple, and finally blue-black, the usual time occupied in these changes being less than five minutes. The print should then be transferred to another dish containing a plain solution of ammoniac sulphocyanate (2 drachms of the salt in 1 pint of water), where it may remain five or ten minutes, after which it should be placed in weak hypo 1—10 until the soluble chloride is dissolved. Ammonium sulphocyanate alone will be found to fix a plate or paper print made with silver citro-chloride emulsion, but hypo is cheaper and quicker. Should the plates or paper be inclined to frill, place them in saturated chrome alum solution after toning; this in no way affects the colour or purity of the whites. Washing is the same as other gelatine plates and silver prints.

Mr. Warnerke informs us that the paper or glass, when heated, keeps whiter if there be free tartaric acid in the emulsion, which we can well believe.

Unwashed Gelatino-Citro-Chloride Emulsion for Printing.

—At a meeting of the London and Provincial Photographic Association, Mr. A. L. Henderson described a modification of the above process: 16 grains of gelatine were swelled in with cold water, and $2\frac{1}{2}$ ounces of distilled water were added. The gelatine was then dissolved by the aid of heat, and $11\frac{1}{2}$ grains of sodium acetate added. To the 42 grains of silver nitrate, dissolved in 1 ounce of water, was next to be stirred in 5 grains of sodium chloride and $7\frac{1}{2}$ grains of sodium citrate, mixed together in 1 ounce of water. Finally, the 1 ounce of gela-

tine, swelled in water, was dissolved and added to the emulsion thus formed, and then water added to make up the bulk of 9 ounces. If the emulsion were required to coat paper, he made up the bulk to half as much again, or double. This emulsion would be used without any washing.

Slow Collodion Emulsion Process for Transparencies.—The following formula has met with approval for the preparation of a collodion emulsion for transparencies, and was one which we used for producing intense negatives: 50 grains of silver nitrate are dissolved in $\frac{1}{2}$ drachm of water, and $\frac{1}{2}$ ounce of boiling alcohol (.805) added. This is poured on 10 grains of pyroxylin, and then 1 ounce of ether added to dissolve the cotton. The silver very probably will precipitate in very fine grains, but this is of no consequence. In another $\frac{1}{2}$ ounce of alcohol, 40 grains of zinc bromide are dissolved, and this solution is gradually added to the above collodion with shaking. Such an emulsion will be found perfectly free from mottling caused by excess of water, and will flow smoothly. When a plate is coated it is washed, and any preservative used (preferably beer), to which to every $\frac{1}{2}$ pint a lump of sugar of the size of a large hazel nut is added.

Slow Gelatine Emulsion.—Slow gelatine emulsion may be prepared by the formula given in Chap. XXXVII., by reducing the time of boiling to five minutes. If emulsification, as described in Chap. XXXVI., be accepted, it will be found that after twelve hours it will be in a condition to give a slow plate. Any emulsion may be made slow by adding 10 grains of copper chloride to it after boiling. These slow plates give wonderful density.

CHAPTER XLVI.

PACKING PLATES.

Packing Gelatine Plates. — The method of packing adopted by some dry-plate makers is an intolerable nuisance. They make zig-zags of thick paper, which they stuff between the ends of each plate, or pair of plates; and when a packet is unclosed and a plate taken out, there is an endless bewilderment of paper and glass, each out of place and hard to put right. Mr. England's plan avoids this, and if the cardboard is smooth, no harm will be done to the plates. He uses little frames of cardboard

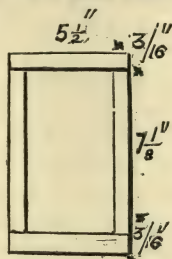


Fig. 17.

to place between his plates, and they are just large enough to be flush with their edges. Thus, for our sized plates ($7\frac{1}{2}$ by 5), we cut strips of card $3\frac{1}{16}$ inches wide, $7\frac{1}{8}$ inches long, and an equal number of strips $5\frac{1}{2}$ inches long.

Tough bank-post paper is gummed over with stiff gum, and allowed to dry, and little squares of about half-inch size cut out. A short piece and a long piece are laid together, on a pair of lines ruled at right angles to one another on a board, and when the square of gummed paper is made to adhere beneath them, and then deftly folded over, two sides of the required frame were made. One more long, and one more short piece, similarly treated, completed the frame. Four-sheet card is what Mr. England recommends. When the strips are cut, we make about thirty of these frames in an hour. The plates are packed alternately back to back and face to face, in the latter case a frame being placed between them.

Our plates are packed in half-dozens, enclosed in two thicknesses of orange paper. The two packets are enclosed in pieces of black varnished paper, and then placed in boxes.

Another plan which we have seen adopted appears to be admirable for smallish sized plates, say up to $8\frac{1}{2}$ by $6\frac{1}{2}$. Four small pieces of card about $\frac{1}{4}$ inch by $\frac{1}{8}$ inch are cut for each alternate plate. After moistening one side, they can be made to adhere to the margins of the plate, thus spreading the two plates which are face to face, by an interval of the thickness of the card; and before placing the plate in the slide, the strips are removed by a pen-knife.

For large sized plates, we believe nothing better than to place moderately stout orange packing paper cut to the size of the plate between each pair. The orange paper, as far as we have seen, has no deleterious effect on the plates.

Boxes made of stiff millboard, and covered with orange paper, are useful. The cover should cover both the top and sides of the box. They should not be too small, but be 1 inch longer and $\frac{1}{2}$ -inch wider, inside measurement, than the plates. A depth of $1\frac{1}{2}$ inches will then take one dozen plates.

Packing Collodion Emulsion Plates.—These plates are even more difficult to pack than gelatine plates. Mr. England's masks can be adopted. Dry plate boxes with grooves are, however, what we prefer to all other plans. The drawback to them is that they are rather bulky.

Note-Book for Registering Plates.—In making an expedition during which plates cannot be developed, or when only some can, it is advisable to enter in a note-book all details. We give an extract from a note-book, which will show the form we recommend. It must be premised, however, that each plate, besides bearing the number of the batch, should also bear a distinctive number, which, for convenience, may be written on the same label as that indicating the batch, but using a red pencil instead of blue.

When the slides are filled before starting, the columns filled up are 4, 5, 6, 7, and the rest are filled up after exposure and after development. By adopting this plan a complete record of every plate exposed and developed is obtained, and will be found of use in judging exposures.

| Date. | Hour. | Light. | Slide. | Batch. | Sensitometer Number. | Number of Plate. | Lens. | Stop. | Exposure. | Subject | Developed. | Developer. | Remarks. |
|---------|-------|--------|--------|--------|----------------------|------------------|-------|-------|----------------------|-----------------------------------|------------|------------|--|
| 18/6/81 | 2.30 | G | 3 | 98 | 26 | 13 | WA* | 3 | 10 sec. | River Arun, looking towards mill. | 20/6/81 | FO | Use of bromide required in developing. |
| " | 3.10 | Cloudy | 4 | 98 | 26 | 14 | RR† | 3 | Inst. 3-inch opening | Lake near Arundel, from south. | 20/6/81 | FO | Detail in dark trees of island fairly out. |
| " | " | " | 5 | 98 | 26 | 15 | " | " | " | " | " | " | " |
| " | " | " | 6 | 98 | 26 | 16 | " | " | " | " | " | " | " |
| " | " | " | 7 | 82 | 18 | 31 | " | " | " | " | " | " | " |
| 18/6/81 | 2.35 | G | 8 | 82 | 18 | 32 | WA* | 2 | 30 | Same as 13. | 20/6/81 | FO | Hypo. used in developer. Detail fair. |

* WA means Dallmeyer's Wide-Angle landscape lens.

† RR means Dallmeyer's Rapid Rectilinear lens.

Weights and Measures.

| | | | | |
|-------------------------------------|-------|---------------|---------------|-------------------|
| 1 Sovereign weighs | ... | ... | ... | 123·274 grains |
| 1 Shilling | „ | ... | ... | 87·273 „ |
| 48 Pence | „ | ... | ... | 1 lb. avoirdupois |
| Half-penny and three-penny piece | weigh | $\frac{1}{4}$ | ounce | |
| Florin and sixpence | ... | ... | $\frac{1}{2}$ | „ |
| Three pennies | ... | ... | 1 | „ |
| 4 half-crowns and 1 shilling | ... | ... | 2 | ounces |
| 4 Florins, 4 half-crowns, 2 pennies | ... | 4 | „ | |
| 1 Half-penny = 1 inch in diameter | | | | |

AVOIRDUPOIS WEIGHT.

| | | | |
|-------------------------------|-----|-----|--------------------------------------|
| 27 $\frac{11}{32}$ Grains ... | ... | ... | 1 drachm (= 27 $\frac{11}{32}$ grs.) |
| 16 Drachms ... | ... | ... | 1 ounce (= 437 $\frac{1}{2}$ „) |
| 16 Ounces ... | ... | ... | 1 pound (= 7000 „) |

TROY WEIGHT.

| | | | |
|-----------------|-----|-----|-----------------------------|
| 24 grains ... | ... | ... | 1 pennyweight (= 24 grains) |
| 20 pennyweights | ... | ... | 1 ounce (= 480 „) |
| 12 ounces... | ... | ... | 1 pound (= 5760 „) |

OLD APOTHECARIES' WEIGHT (superseded in 1864).

| | | | |
|----------------|-----|-----|-------------------------|
| 20 Grains ... | ... | ... | 1 scruple (= 20 grains) |
| 3 Scruples ... | ... | ... | 1 drachm (= 60 „) |
| 8 Drachms ... | ... | ... | 1 ounce (= 480 „) |
| 12 Ounces ... | ... | ... | 1 pound (= 5760 „) |

The New Apothecaries' Weight is the same as Avoirdupois.

LIQUID MEASURE.

| | | | |
|---------------|-----|-----|---------------------------------|
| 60 Minims ... | ... | ... | 1 drachm |
| 8 Drachms... | ... | ... | 1 ounce = 1·73 cub. ins. nearly |
| 20 Ounces ... | ... | ... | 1 pint = 34·66 „ „ |
| 8 Pints ... | ... | ... | 1 gallon = 277·25 „ „ |

The Imp. Gallon is exactly 10 lbs. Avoir. of pure water ; the pint, 1 $\frac{1}{4}$ lbs.

FLUID MEASURE.

| | |
|--------------------------|-----------------------------|
| 1 Minim = 1 drop | 2 Drs. = 1 dessert spoonful |
| 1 Drachm = 1 teaspoonful | 4 „ = 1 table „ |

FRENCH MEASURES.

| | |
|-------------------------------|---|
| 1 Gramme ... | 15·432 grains |
| Kilogramme ... | 1000 grammes (= 2·2 lbs. Avoir. nearly) |
| 1 Litre ... | 35·216 ounces (fluid) |
| 1 Cubic Centimetre (c.c.) ... | 17 minims nearly |
| 50 Cubic Centimetres ... | 1 ounce 6 drachms 5 minims |
| 1 Metre... | 39·37 inches |



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